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AN ATLAS OF GAS CHROMATOGRAMS OF OILS USING DUAL FLAME-IONIZATION AND NITROGEN PHOSPHORUS DETECTORS

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16. Abstract

The report details experimental techniques for using a thermionic nitrogen phosphorus detector (NPD) for gas chromatographic (GC) "fingerprinting" of petroleum and synthetic oils. An alumina column chromatography procedure for isolating and concentrating the compounds in this "N-fingerprint" is described.

Dual FID-NPD detector GC curves of over 70 assorted petroleum crudes and distillates run on a 50-foot Dexsil-300 SCOT column are reproduced to form a reference atlas for comparitive purposes. The data in the atlas indicate that this detector combination can be useful for oil fingerprinting, and research in organic geochemistry and oil pollution and combustion products.

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METRIC CONVERSION FACTORS

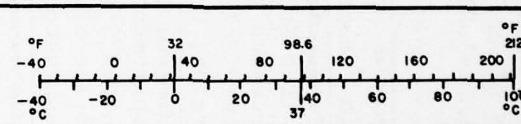
Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.

Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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INTRODUCTION

A wide variety of instrumental analytical techniques have been brought to bear upon the problem of identifying and characterizing oils (1). Since oils are complex mixtures of very large numbers of organic compounds, gas chromatography (GC), with its unparalleled separation efficiency, is especially suitable for characterizing the components of the mixture. It is one of the four techniques used by the United States Coast Guard Research and Development Center's (R&DC) oil spill identification system (2, Appendix D). The primary detector is the flame ionization detector (FID), which gives a sensitive response to all carbon compounds. The column effluent is also split to a flame photometric detector (FPD) whose response is tuned to the 394-nm emission of S_2 in a hydrogen-air flame to provide a highly sensitive and selective response to organic, sulfur-containing compounds. With the use of a support-coated open-tubular (SCOT) column and carrier make-up gas, these detectors provide two detailed independent "fingerprints" of an oil sample from a single chromatographic run.

Another sensitive, element-selective detector which might be employed in a similar fashion to the FPD to obtain an independent fingerprint is the nitrogen-phosphorus detector (NPD). We recently reported (3,4) preliminary experiments on the use of such a detector for oil fingerprinting. These experiments indicated that the NPD shows some promise for use in oil fingerprinting as well as other aspects of petroleum chemistry such as geochemical research and pollution evaluation.

The purposes of this report are as follows: (a) To describe in greater detail the experimental procedures we used in employing the GC-NPD system for oil analysis to enable other researchers to reproduce our methods. (b) To provide an atlas of some seventy dual FID-NPD GC traces from a wide variety of oil types and sources to allow petroleum chemists and oil identification experts to obtain a comparative overview of both the FID and NPD patterns that can be expected from many common types of oils when standard oil identification system columns are used (2, page D-7).

Data on experience with the GC-NPD system on actual spill case samples and on the effects of weathering on NPD peak patterns in oils will be submitted for publication elsewhere.

EQUIPMENT

Samples were run on a Perkin-Elmer 990 GC equipped with an AS-41 automatic capsule injection system for unattended, splitless, solvent-free injection of the oils. Helium carrier gas was routed through one flow controller to provide carrier make-up gas to the receiver fitting at the effluent end of the column. The eluted components with carrier make-up were then split in a ratio of 1:1 to the FID and NPD detectors using standard stainless steel capillary tubing in the heated manifold compartment of the GC.

With packed columns the carrier gas was flow-controlled at 30 ml/min with an additional 30 ml/min carrier make-up supplied. SCOT columns were pressure-controlled at 16 psig (Column A) or 20 psig (Column B) to give a room temperature flow rate of 3.0 ml/min and a 40 ml/min carrier make-up was supplied. All flows were checked simultaneously at room temperature with a soap bubble flow meter.

Hydrogen and air for the FID and NPD detectors were supplied by a General Electric Model 15EHG2A1 hydrogen generator and an AADCO Model 737 dry-air generator. Gas connections for the detector flames were made according to the manufacturer's instructions with a special plumbing kit supplied with the NPD. In the work reported here the NPD was operated in the "nitrogen-phosphorus mode." Selectivity and sensitivity for N-compounds relative to hydrocarbons were optimized with respect to hydrogen flow rate using the manufacturer's test solution of N, N-dimethylaniline and C8, C9, and C10 normal hydrocarbons. When their conditions of relative signal-to-noise ratios for these compounds are met, a discrimination of at least 100,000 to 1 for the N-compound with respect to the hydrocarbons is claimed. The conditions were met with an air flow rate of 100 ml/min (50 psig) and a hydrogen flow rate of 2.8 ml/min (13 psig "Column B controller"), and these settings were used for all runs reported in this paper. The FID used flow rates of 21.6 ml/min H_2 (20 psig "Column A controller") and an air flow rate of 353 ml/min.

The NPD used is manufactured by Perkin-Elmer and is diagrammed in Figure 1. It consists of a standard FID design operating under conditions of a fuel-poor flame which largely suppresses the normal FID response with the addition of an independently heated rubidium glass bead in the flame which interacts with burning N- and P-containing compounds to give a sensitive and selective thermionic response. The development of this design, and its theory and applications are extensively described in two papers by its inventor, Kolb (5,6). Although the detector is highly selective for compounds containing N or P, there is still a FID response to much larger quantities of carbon compounds. Thus in the case of oils, the NPD may show peaks resulting from this "spurious FID response."

The power supply module for this particular NPD design contains a helical potentiometer to permit fine adjustment of the current supplied to vary the temperature of the rubidium glass bead independently of the effect produced by the flame. The voltage between the jet tip and the collector can be varied by a polarity switch with three settings. Setting 3 provides maximum sensitivity, while Setting 2 results in less sensitivity but greater selectivity for N-compounds. The primary factor which controls the sensitivity of the detector

to N- and P-compounds is the temperature of the bead. This in turn is a complex function of the hydrogen and air flow rates, as well as the carrier gas composition and flow rate. The independent resistance heating of the bead allows both its temperature and the flame combustion conditions to be independently optimized for sensitivity and nitrogen selectivity. The complex interactions of these parameters and their optimization have recently been discussed by Galjch et. al (7). In general, the higher the temperature of the bead, the greater its NPD response will be; but also the more rapid will be its degradation and decline in sensitivity.

Chromatograms were produced on a Perkin-Elmer Model 56 chart recorder. The NPD patterns are displayed inverted above the corresponding FID pattern. Note that the NPD peaks are offset 0.23 min later than corresponding FID peaks to allow the pens to cross without interference.

The results reported in this publication were obtained on four different GC columns which are described in Table I below. The standard column oven temperature program was from 75°C to 300°C at 8°C/min with a final hold of 16-32 min. The injector temperature was 250°C and the manifold and detector blocks were at 330°C.

TABLE I

GC COLUMNS USED IN NPD EXPERIMENTS ON OILS

COLUMN	DIMENSIONS	STATIONARY PHASE	COLUMN MATERIAL
A	15.25m x 0.5mm i.d.	Dexsil 300 SCOT	Stainless Steel
B	36m x 0.5mm i.d.	SE-30 SCOT	Glass
C	3m x 3mm o.d.	3% OV-101 on 80/100 Gas Chrom Q	Stainless Steel
D	1.8m x 2mm i.d.	3% OV-17 on 100/120 Chromosorb WP	Glass

EXPERIMENTAL TECHNIQUES

Figure 2 shows the dual FID-NPD chromatograms of a light fuel oil obtained on Column C using the standard temperature program. It is important to use this simultaneous dual detection procedure, not only to maximize information content from a run but also to detect any spurious FID response in the NPD pattern. In Figure 2A, the pattern of large NPD peaks is a group of N-compounds, while the preceding smaller peaks are due to the FID response that appears when using Polarity Setting 3 for maximum sensitivity. Figure 2B shows that the sensitivity is decreased (note attenuations used) when Polarity Setting 2 is used. However, the spurious FID response is repressed, and one can distinguish the N-compound pattern with much more confidence.

Some oils have very low concentrations of N-compounds which would require the use of large sample volumes and maximum sensitivity operation of the detector. Under these conditions, the FID response would hopelessly confuse the nitrogen fingerprint. It would be desirable to have a separation procedure to isolate the peaks which produce the NPD fingerprint from the overwhelming mass of hydrocarbons producing the FID response. The majority of the N-compounds in oils which are providing the NPD fingerprint are probably N-heterocycles or aromatic amines (8,9). Simple extractions probably will not completely separate these compound classes from the wide variety of hydrocarbons present in an oil. Alumina column separations have a greater ability to separate compound classes distinctly in a single pass, and this is the technique we investigated to isolate the NPD fingerprint.

Alumina Column Separation Procedure

The procedure is outlined in the flow chart of Figure 3. Brockman neutral activity Grade #1 alumina (Fisher Scientific Company) was calcined for 18 hours at 200°C, cooled in a dessicator, and partially deactivated by shaking in a large Erlenmeyer flask with 5 percent by weight of distilled water. Small "tulip" columns 20 cm by 0.5 cm i.d. of glass with integral 50 ml solvent reservoirs and Teflon stopcocks (from Scientific Glass Apparatus) were filled with chromatoquality n-pentane and let stand one-half hour until degassing ceased. A small glass wool plug was inserted above the stopcock and a n-pentane slurry of 3.80 g of alumina was allowed to fill the column by sedimentation. Pentane was drained from the column until only a 5 mm layer remained above the alumina bed.

Fifty microliters of the heated oil sample was dispensed into the superficial pentane layer from a precalibrated disposable Pasteur pipet. The pipet was rinsed by pumping the resulting solution with the bulb, and the stopcock of the column was opened to load the oil solution onto the top of the alumina bed. The top of the column above the bed was rinsed with small additions of pentane to transfer all of the oil to the top of the bed (the oil color will be observed in the top 2-4 cm of column packing).

Elute with 6.0 ml pentane, replace solvent in reservior with benzene (CAUTION - carry out procedure in fume hood!) and continue elution until evidence of color or solvent mixing in the column tip is seen. Remove the pentane fraction for concentration and analysis if desired. It contains aliphatics, some aromatics,

FIG. I PERKIN-ELMER NPD

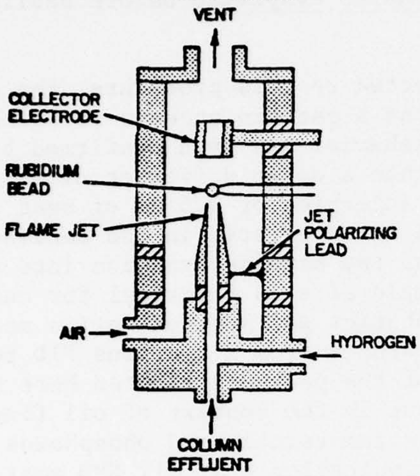


FIG. 2 TRIGOM NO. 2 OIL
ON COLUMN C

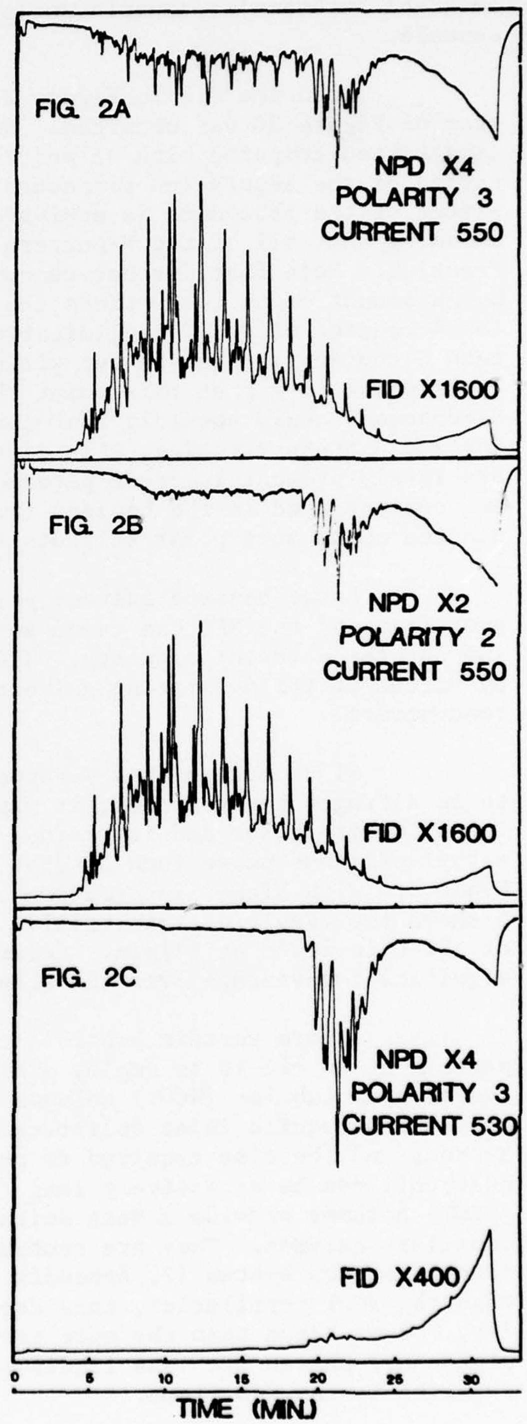
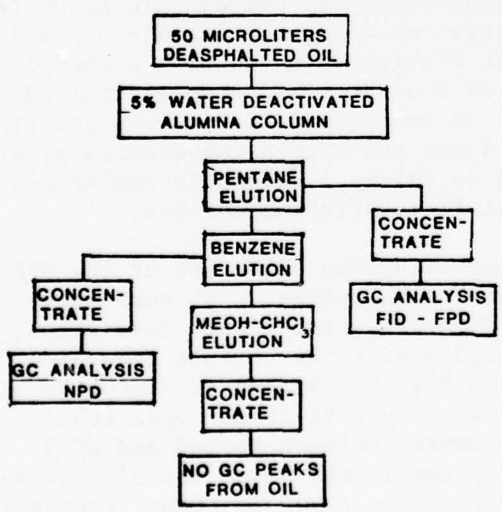


FIG. 3 ALUMINA COLUMN SEPARATION
PROCEDURE FLOWCHART



and most of the sulfur-containing organic compounds. Collect the first 3 ml of benzene eluant in a precalibrated (1.0 ml and 3.0 ml) glass vial (with a Teflon-lined cap) and concentrate under a stream of dry nitrogen on a hot plate to a volume of 1.0 ml. Take 10 ul of the concentrated benzene fraction and load into an AS-41 autosampler capsule and allow benzene to evaporate before sealing the capsule.

When the oil in Figure 2 was subjected to this procedure, the chromatogram of Figure 2C was obtained. Note that the N-pattern appears to be extracted intact when compared with 2A and 2B. This behavior has been confirmed by application of the separation procedure to more than a dozen different oils. The effect of the procedure is equivalent to an injection of 0.5 ul of neat oil assuming that all of the N-pattern compounds are recovered in the benzene fraction. Note that further concentration of the benzene fraction into capsules by an amount of up to 50 times the above sample size is practical for cases of low N-content oils. The elimination of aliphatics and most aromatics means that such a concentrate can be run without interference from a spurious FID response. It is worth noting at this point that some of the peaks attributed here to N-compounds could possibly be P-compounds, but in the context of oil fingerprinting and pattern matching, this distinction is immaterial, and phosphorus compounds are rarely present in crude petroleums. An indication that all NPD active peaks are concentrated in the benzene fraction is the absence of any in subsequent eluates using more polar solvents such as methanol and chloroform.

Large benzene solvent peaks eluting from the GC column into the fuel-poor flame of the NPD can cause soot and carbon fiber formation, possibly shorting out the detector elements. Thus the capsule injection system is valuable by virtue of its permitting solvent-free introduction of the benzene-fraction concentrate.

Since many of the N-compounds seen in the NPD pattern are suspected to be nitrogen heterocycles, it might be that replacing the stainless steel Column C with glass and its methyl-silicone stationary phase with a phenyl-methyl-silicone phase such as that of Column D might yield a more detailed N-pattern with higher information content. A comparison of Figure 4 and Figure 5 shows the result of this trial. Figure 5 was run with a temperature program of 190°C to 280°C at 6°/min. Columns such as Column D evidently confer no significant advantage over the standard oil fingerprinting columns.

A more certain possibility for improving the structure of the NPD pattern of an oil is to employ a higher resolution column. Although wall-coated open tubular (WCOT) columns are capable of extraordinary resolution, they often require inlet splitters incompatable with the capsule injection system, and the time required to produce the high resolution chromatogram of a heavy oil can be excessively long (2-3 hours). Support-coated open tubular (SCOT) columns provide a very suitable compromise between packed and WCOT capillary columns. They are recommended for use in the Coast Guard's oil spill identification system (2, Appendix D). They can be taken to higher temperatures than the WCOT capillaries, thus decreasing the analysis time. They produce less column bleed than the more heavily loaded packed columns, and thus silicone stationary phases are less likely to deactivate the rubidium bead with silica deposits in the NPD flame.

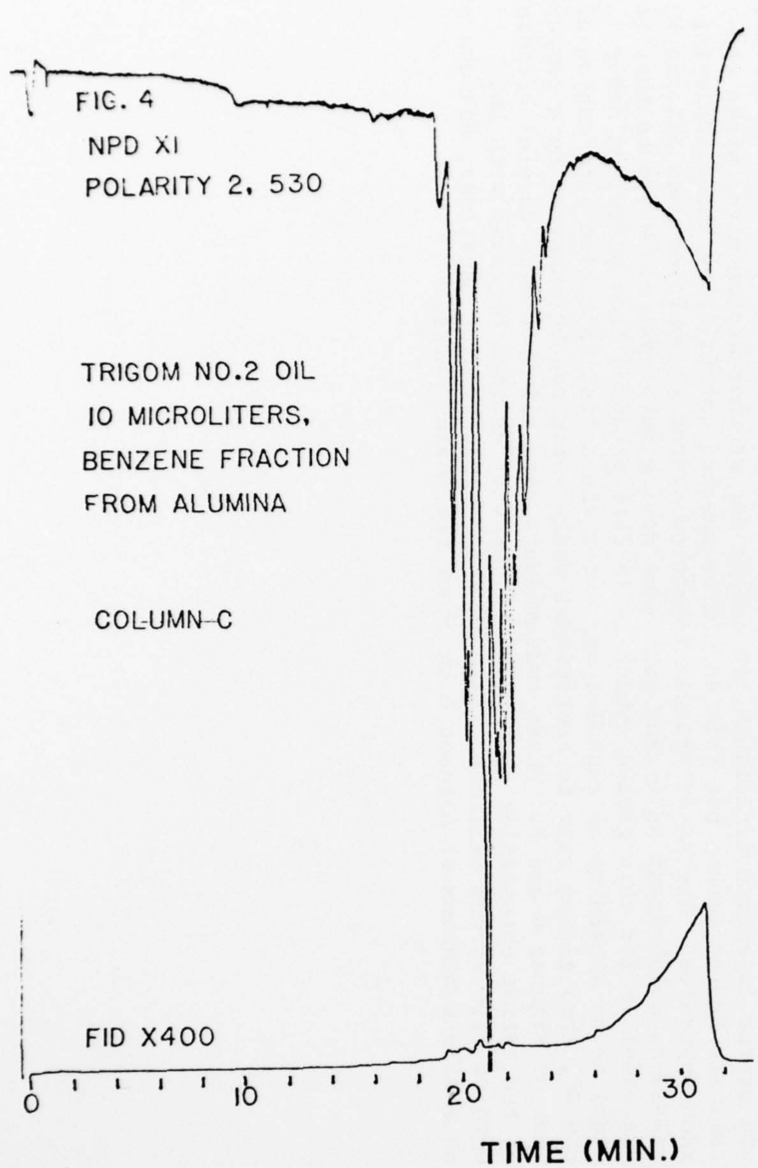


FIG. 4
NPD X1
POLARITY 2, 530
TRIGOM NO.2 OIL
10 MICROLITERS,
BENZENE FRACTION
FROM ALUMINA
COLUMN-C
FID X400
0
10
20
30
TIME (MIN.)

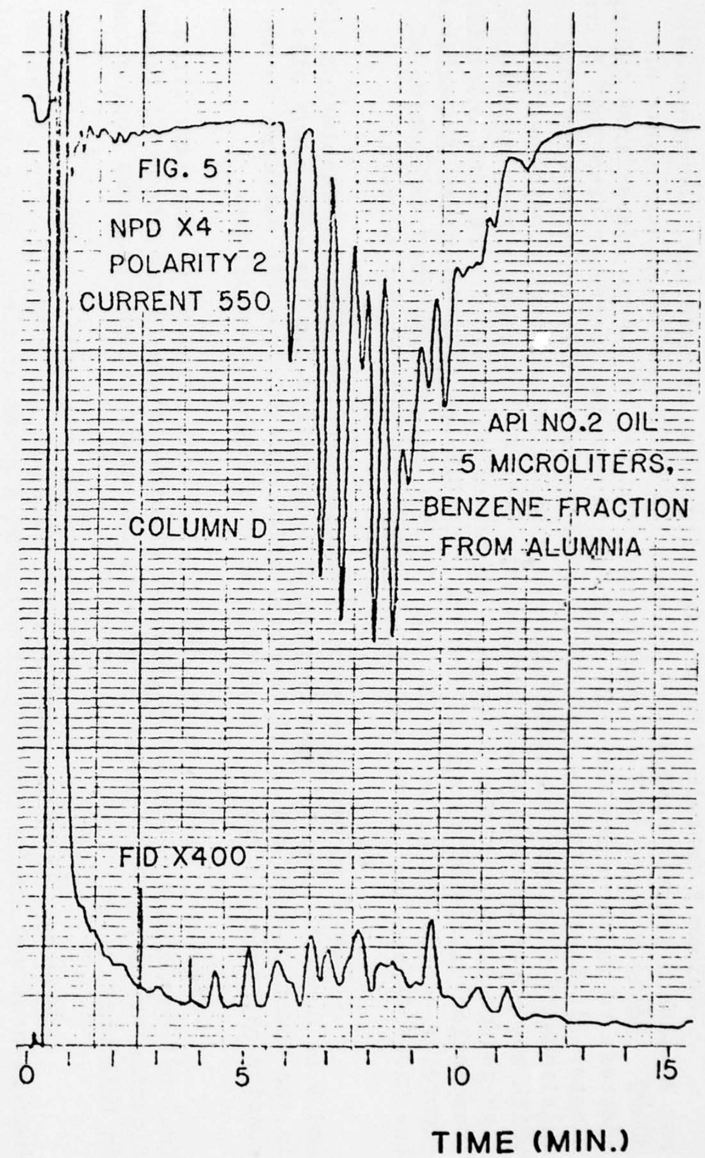


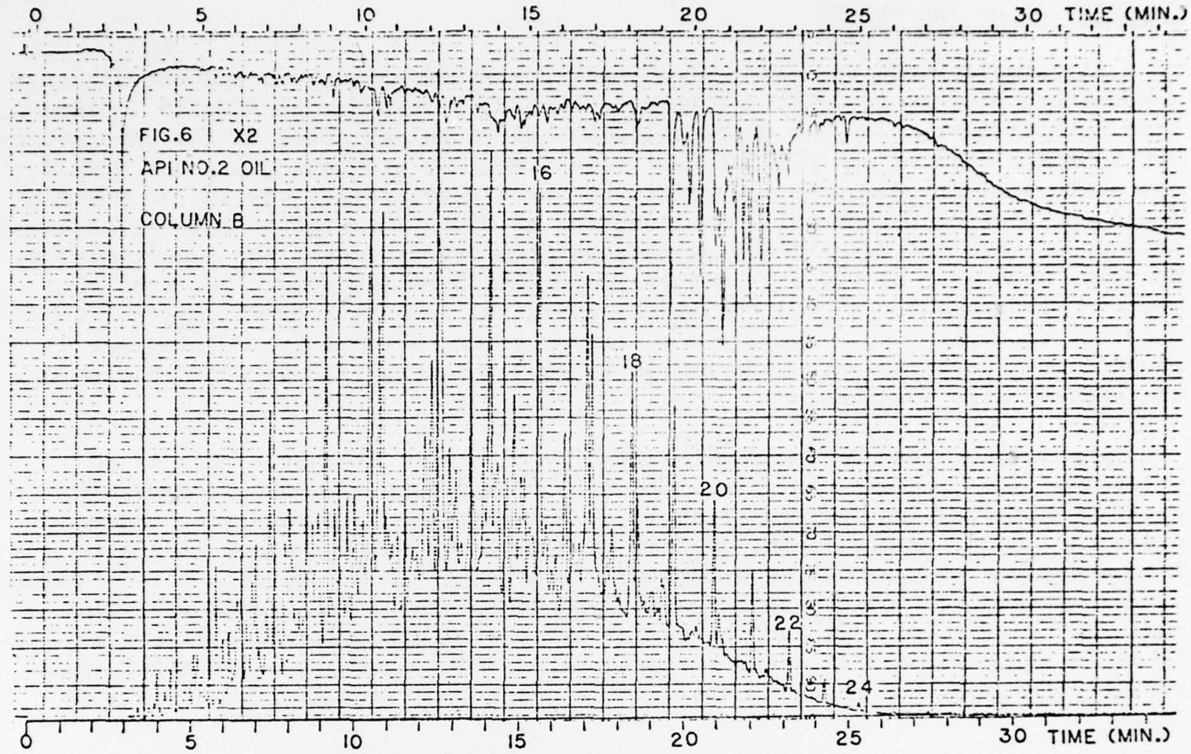
FIG. 5
NPD X4
POLARITY 2
CURRENT 550
COLUMN D
API NO.2 OIL
5 MICROLITERS,
BENZENE FRACTION
FROM ALUMNIA
FID X400
0
5
10
15
TIME (MIN.)

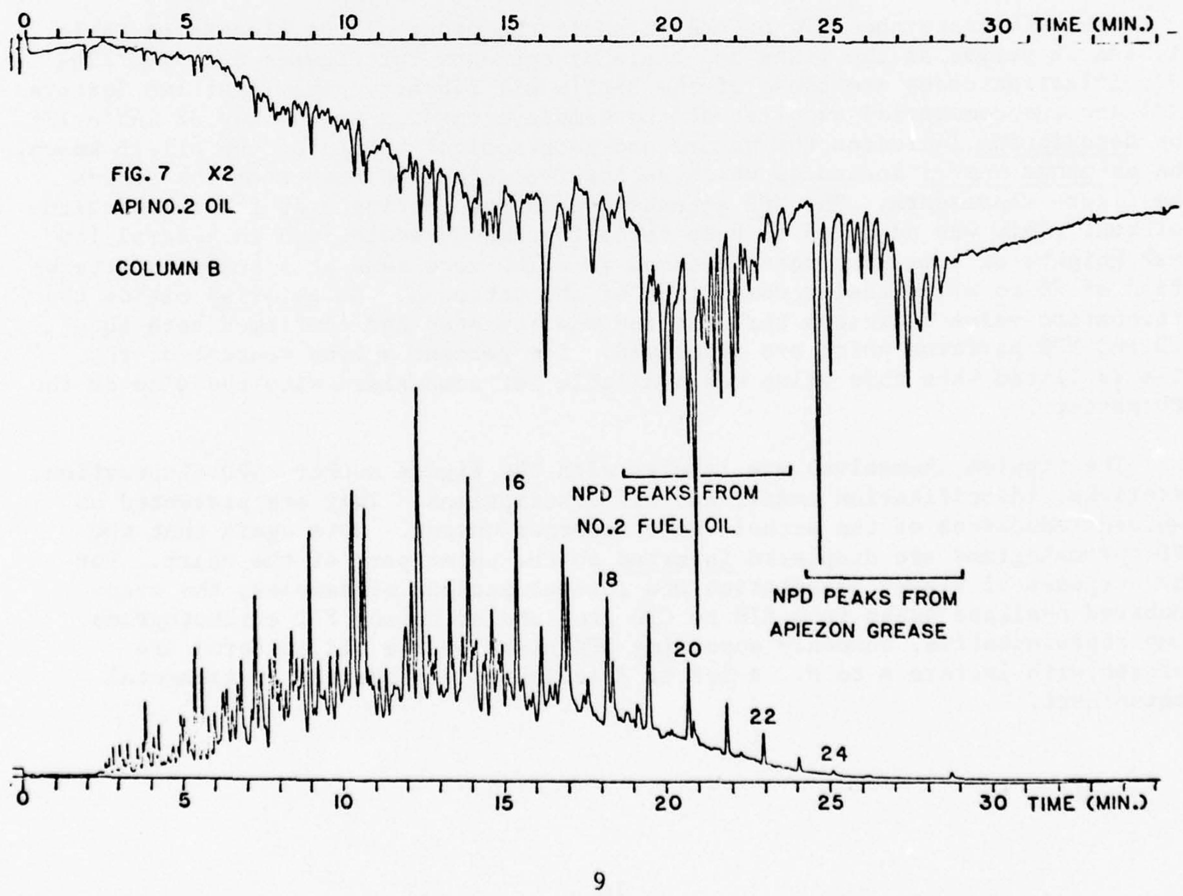
Column B (obtained from Scientific Glass Engineering, Incorporated) was a Class B (normal resolution) column with a theoretical plate number of 30300. Being a glass SCOT column, it required use of 0.4-mm glass-lined tubing adapters to injector and detector fittings, and rather delicate graphlok[R] ferrule adapter fittings to the column. Leak checking is usually required with this multitude of fittings, and many leak-check solutions contain phosphorous compounds which may enter the system and contaminate the NPD response, giving anomalously high column bleed. On the other hand, this column provided excellent resolution (resolution values of 13 and 11 for the C16, C18 and C18, C20 pairs respectively, according to the criterion of (2, page D-12). It also provided resolution of the C17-Pristane and C18-Phytane pairs in the FID hydrocarbon pattern.

Column A is metal, easier to handle, provides adequate resolution (11 and 9 as described above), and is presently specified for use with heavy oils in the Coast Guard's oil spill identification system. Its FID patterns do not resolve pristane and phytane from C17 and C18 normal hydrocarbons.

Figures 6 and 8 compare the FID-NPD peak patterns of the same light fuel oil on Columns B and A. Because of Column A's use in the oil spill identification system, it was chosen to provide the atlas of chromatograms reproduced in this work.

When one is using a GC detector with the great sensitivity of the NPD, instrumental and sample contamination can be a great problem. Since we did not use septum injection techniques, we cannot say whether septum bleed might contaminate NPD patterns, but this should be checked carefully by those employing such apparatus. The AS-41 capsule injection system we employed uses Apiezon M grease as a lubricant on O-ring seals and moving metal parts. We found that it was possible for this grease (which is in fact produced from petroleum heavy ends) to be picked up on capsules and enter the heated injection port region of the GC, thus giving rise to contaminant peaks which can be observed by a comparison of Figures 6 and 7. These contaminants were eliminated by careful cleaning of the entire autosampler system, replacement of Apiezon M grease with Dow-Corning High Vacuum Silicone grease on the capsule-holding magazines, and use of an absolute minimum of Apiezon M on other key moving parts.


0 5 10 15 20 25 30 TIME (MIN.)
FIG.6 X2
API NO.2 OIL
COLUMN B
16
18
20
22
24
0 5 10 15 20 25 30 TIME (MIN.)


0 5 10 15 20 25 30 TIME (MIN.)
FIG. 7 X2
API NO.2 OIL
COLUMN B
NPD PEAKS FROM
NO.2 FUEL OIL
NPD PEAKS FROM
APIEZON GREASE
16
18
20
22
24
0 5 10 15 20 25 30 TIME (MIN.)

DESCRIPTION OF THE SURVEY

All samples were run using previously described parameters and the standard temperature program on a 15.25-m Dexsil-300 SCOT column Serial #SC3710 (Column A) from Perkin-Elmer. The FID attenuation was X1600 unless noted on the chromatogram. The rubidium bead of the NPD had been conditioned by previous daily use over a one-month period. The polarity switch of the NPD controller was set at Position 2 and the heating current at a dial setting of 560. This latter setting does not produce as much NPD sensitivity as is possible, but it caused the sensitivity to decrease much more slowly than higher, more sensitive settings. The samples were run continuously around the clock, using the automatic AS-41 injector over a period of eight days. Samples with inappropriate attenuation settings or suspect peak patterns were repeated until good chromatograms or confirmation of the pattern were obtained.

The samples were drawn from the R&DC's oil sample library. This is an extensive file of crude and distillate oils provided by various oil companies together with varying degrees of physical and chemical documentation. Additionally, the unweathered oil samples from the TRIGOM weathering study (10) were included since they have been extensively studied. Other reference oils, several cargo samples from notable spill cases, and four "synthetic" crudes were also run. The classes of oils and the number of oils in each class are listed in Table II. The volumes injected for each class and the sample preparation (neat sample or deasphalted (DDS) according to 2, page D-5) are also listed in this table.

Table IV lists the oils of the atlas in the order of the classes of Table II, and it serves as the index and table of contents for Figures 8 to 79. The identification codes are those of the R&DC's oil library. The first two letters indicate the commercial supplier of the sample according to the key of Table III. The description indicates the nature and geographical origin of the oil if known. The sequence number indicates which successive injection number of the series the figure represents. The NPD attenuation is the setting used for the particular run. This was adjusted to keep chromatograms on scale, and in general low peak heights on some runs were accepted to allow more runs at a standard attenuation of X8 to allow easier comparison of the patterns. An asterisk beside the attenuation value indicates that the run was repeated and confirmed both the FID and NPD patterns which are displayed. The percent sulfur content of the oils is listed when this value was available for comparison with the size of the NPD pattern.

The figures themselves are labeled with the figure number, NPD attenuation, asterisks, identification codes, and oil descriptions. They are presented as twofold reductions of the actual chart recorder output. Note again that the NPD chromatograms are displayed inverted on the upper part of the chart. For the purposes of viewer orientation and intercomparison of samples, the even-numbered n-alkane peaks from C16 to C30 are labeled on the FID chromatograms. Some representative, commonly appearing NPD peaks in the oil patterns are labeled with letters A to H. A letter X indicates a suspected instrumental contaminant.

TABLE II

CLASSES OF OIL SURVEYED IN THE FID-NPD GC ATLAS

NUMBER OF SAMPLES RUN	DESCRIPTION OF OIL CLASS	VOLUME INJECTED (microliters)	PREPARATION
9	Light Oils (No. 2 and diesels)	0.25	Neat
11	Intermediate Distillates (No. 4)	0.25*	Neat*
10	Heavy Distillates (No. 5, 6 and Bunkers)	0.5	DDS
1	Lubricating Oil	0.5	DDS
4	Synthetic Crudes	0.5	DDS
15	Domestic Crudes	0.5	DDS
22	Foreign Crudes	0.5	DDS

*Figure 27 = 0.5 ul, Figures 17, 20, 21, 27 = DDS

TABLE III

KEY TO OIL COMPANY IDENTIFICATION CODES FOR R&D CENTER OIL LIBRARY

AM	Amoco	GU	Gulf
AR	Atlantic Richfield	IN	Independent
AS	Ashland	SH	Shell
CH	Chevron	ST	Sohio
CO	Conoco	SU	Sunoco
EP	E.P.A. (U.S. Government)	TX	Texaco
EX	Exxon	UN	Union

TABLE IV

OILS OF THE FID-NPD ATLAS

FIGURE NUMBER	PAGE NUMBER	I.D. CODE	DESCRIPTION	SEQUENCE	NPD ATTENUATION	PERCENT SULFUR CONTENT
			LIGHT DISTILLATES			
8	18		API No. 2 Oil	1	X2	--
9	18		TRIGOM No. 2 Oil	81	X2*	--
10	19		API T-3 No. 2 Oil	3	X2*	--
11	19	AR-013-D02	Navy Marine Diesel	4	X2	0.42
12	20	EX-011-F02	N.J. Heating Oil	5	X2	0.13
13	20	GU-031-F02	No. 2 Oil	6	X2	0.07
14	21	AM-035-F02	Marine Diesel Fuel	7	X2	0.44
15	21	GU-075-MOD	Heavy Marine Diesel	8	X2	--
16	22	AM-033-F00	Special Fuel	99	X8*	1.39
			NO. 4 OILS			
17	22		TRIGOM No. 4 Oil	11	X2	--
18	23	SU-021-F04	No. 4 Oil	83	X2	0.37
19	23	UN-004-F04	No. 4 Oil	84	X2	0.85
20	24	EX-079-F04	No. 4 Oil	16	X4	0.05
21	24	AM-044-F04	No. 4 Oil	17	X4	0.94
22	25	EX-019-F04	No. 4 Oil	18	X4	0.05
23	25	IN-016-F04	No. 4 Oil	19	X4	--
24	26	EX-059-F04	No. 4 Oil	74	X4*	0.05
25	26	ST-011-F04	No. 4 Oil	14	X8*	--
26	27	CH-008-F04	No. 4 Oil	15	X8	1.14
27	27	CH-011-F04	No. 4 Oil	75	X8*	1.14
			No. 6 OILS AND BUNKERS			
28	28	AR-004-F00	Navy Special Fuel	76	X32*	2.00
29	28	GU-060-X0X	Pale Oil	32	X8	--
30	29	EX-007-F06	Desulfurized No. 6 Oil	36	X8	0.27
31	29	EX-008-F06	Bunker Fuel No. 6 Oil	42	X8	2.04
32	30		TRIGOM No. 6 Oil	51	X8	--
33	30		ARGO MERCHANT Cargo	52	X8	--
34	31		GRAND ZENITH Cargo	53	X8	--
35	31	GU-046-MBC	Venezuelan Bunker C	54	X8	--
36	32	AM-029-F05	No. 5 Oil	77	X32*	1.48
37	32		API Bunker C	78	X64*	--
			LUBRICATING OIL			
38	33	EX-010-LOM	Marine Lube	69	X8	--
			SYNTHETIC OILS			
39	33		Bunker C From Parahoe Shale	80	X64*	--
40	34		West Kentucky Syncrude (From Coal)	71	X64	0.08
41	34		Bureau of Mines Synthoil (From West Virginia Coal)	72	X64	0.42
42	35		Utah Syncrude (From Coal)	79	X64*	0.05
			DOMESTIC CRUDES			
43	35		API T-1 Louisiana	22	X8*	
44	36	GU-014-CGU	Offshore S. Louisiana	30	X8*	0.32
45	36		TRIGOM Louisiana Crude	48	X8*	

TABLE IV (continued)

FIGURE NUMBER	PAGE NUMBER	I.D. CODE	DESCRIPTION	SEQUENCE	NPD ATTENUATION	PERCENT SULFUR CONTENT
			DOMESTIC CRUDES (continued)			
46	37	GU-035-CDO	West Texas Semi-Sweet	50	X8	0.39
47	37	GU-042-CDC	West Texas Sour Crude	56	X8	1.86
48	38	GU-055-CDO	Alabama Citronelle	38	X8	0.38
49	38	GU-015-DCO	Florida (Jay Smackover)	61	X8*	
50	39	EP-001-CDO	Illinois Basin, Wayne Company, 5420 Feet	37	X8	
51	39	EP-002-CDO	Illinois Crude, Jasper Company, 100 Feet	43	X8	
52	40	AS-008-CDO	Illinois Crude	47	X8	
53	40	GU-057-CDO	Pennsylvania Crude	33	X8	
54	41	AS-007-CDO	Eastern Kentucky	63	X8*	
55	41	TX-005-CDO	Utah, Rocky Mountains Altamont Crude	62	X8	
56	42	AM-007-CDO	Wyoming, Dead Horse Creek	65	X8*	0.14
57	42	EX-029-CDO	California, San Joaquin	66	X8*	
			IMPORTED CRUDES			
			Middle East			
58	43	TX-029-CME	Iranian Crude	24	X8	--
59	43	SH-034-CME	Iranian Crude	41	X8	--
60	44	CO-002-CME	Iranian Light	44	X8	1.45
61	44	AS-006-CME	Iranian Sassan Crude	45	X8	--
62	45		70113 Gach Saran Iranian	49	X8	--
63	45	GU-008-CME	Kuwait Crude	25	X8*	2.52
64	46	TX-027-CME	Arabian Crude	26	X8*	1.70
			Venezuelan			
65	46	CH-013-CVE	W. Venezuela Boscan (Lake Maracaibo)	28	X8*	--
66	47	CO-013-CVE	Venezuela, Anaco	34	X8	0.18
67	47	GU-078-CSA	S. America, Anaco Wax	67	X8*	--
68	48	CO-014-CVE	Venezuela, Blend of Lagatreco and Bachaquero	57	X8	1.48
69	48		70025 Venezuelan Bachaquero Crude	59	X8*	--
70	49	EX-022-CEC	Ecuador, Oriente	44	X8	--
71	49	AM-037-CTR	Trinidad Crude	60	X8	0.29
72	50	AM-004-CAF	Algeria, Arzew	29	X8*	0.10
73	50		69069 Egypt, El Morgan	55	X8*	--
74	51	AM-001-CAU	Australia, Hallbut	64	X8	0.12
75	51	EX-021-CFR	Indonesia, Ardjuna (Offshore Blend)	35	X8	--
			ALASKAN			
76	52	EX-019-CAL	Alaska, Prudhoe	21	X8*	--
77	52	CO-012-CAL	Alaska, North Slope	23	X8*	1.01
78	53		71011 Prudhoe Bay	58	X8	--
79	53	CO-011-CEU	North Sea, Ekofisk	68	X8*	0.21

DISCUSSION OF NPD RESULTS OF THE SURVEY

Many oils which showed substantial NPD peak patterns appeared to contain many of the same nitrogen compounds, as judged by matching retention times of the peaks. Retention time (t_r) is not a sufficient condition of peak identity, but it seemed probable that many of the peaks seen were the same compounds since they were consistently observed in many different oils. Table V lists the retention times and indices of many but not all of the peaks often seen in the oils. The retention times are chosen for runs made during the middle of the series. These t_r's tended to vary somewhat over the course of the experiments, and a more reproducible value was the retention index (RI). This value was not calculated in the rigorous fashion defined by Kováts for isothermal GC, but was estimated by linear interpolation of the retention times of the NPD peaks with respect to those of the bracketing n-alkane spurious FID response peaks on the same runs. This is moderately accurate for linear temperature programmed runs over the range of C20 to C30 n-alkane retention times, which were approximately evenly spaced. The presence of n-alkane peaks in most of the oils, combined with the spurious FID response in the NPD chromatogram facilitated this measurement and calculation. Most NPD patterns in the oils consisted of an "early pattern" (Peaks 1-19 between RI = 2000-2600) of large well-resolved peaks, and a "late pattern" (Peaks 20-29 between RI = 2600-3000) of smaller, broader peaks which are often superimposed on an unresolved NPD response.

The following notes list some general impressions and comments pertaining to the NPD patterns by oil class.

No. 2 Oils - Some are very similar, some are different; the total size differs considerably, only the early pattern is seen, as if the late pattern were removed by refining.

No. 4 Oils - A great variety of patterns was seen, possibly due to the intermediate nature of the refining and blending processes described by this class.

No. 6 Oils and Bunkers - Patterns were very large and distinctive, as would be expected since this fraction from the refining process should concentrate the heavy N-heterocyclic compounds.

Lube Oil - No NPD patterns were seen in this and other unused lube oils. This is expected since such oils are processed to remove as much nitrogen content as possible. Work by Lee et. al (11) using capillary GC with NPD detection has shown NPD patterns in motor oils after long engine operation, which appear to be specific to the operating conditions of individual engines.

Synthetic Oils -

Figure 39 - This shale-oil derived bunker C product displays a very intriguing series of NPD peaks (not spurious FID response), which suggest the presence of an homologous

TABLE V

NPD PEAKS, PATTERNS

PEAK NUMBER	LETTER	t_r (min)	RI	
1	A	21.35	2080	
2		21.60	2100	
3		21.75	2110	
4	B	21.10	2140	
5		22.55	2180	
6	C	22.80	2200	
7		23.15	2230	
8		23.25	2240	
9		23.40	2255	EARLY
10	D	23.60	2275	PATTERN
11		23.87	2300	
12		23.95	2310	
13		24.20	2330	
14		24.45	2355	
15	E	24.60	2370	
16		25.15	2420	
17	F	25.37	2440	
18		25.95	2500	
19		26.30	2535	
20		27.05	2610	
21		28.00	2710	
22		28.60	2775	
23		29.25	2840	
24		29.80	2890	LATE
25		30.15	2925	PATTERN
26	G	30.80	2980	
27		31.25	3020	
28	H	31.60	3040	
29		31.70	3050	

series of N-compounds. Note a report by Blumer (12) which describes the detection of such series by mass spectroscopy in recent marine sediments.

Figure 40 - 0.23% nitrogen (13)
Figure 41 - 0.79% nitrogen (14)
Figure 42 - 0.478% nitrogen (15)

The above coal-derived oils show very large NPD patterns, which are completely unrelated to the usual petroleum-derived patterns. This may result from reactions occurring during the synthesis procedure. A recent paper by Schiller (16) describes the identification of several of these nitrogen compounds from a similar oil by GC-MS procedures, and he describes several reasons why knowledge of the nature the N-compound content is necessary.

<u>Crude Oils</u> - The NPD patterns can differ considerably, but patterns of oils from the same geographic area are often quite similar. Louisiana crudes (Figures 43, 44, and 45) showed very low NPD patterns, and the oils of Figures 48, 49, 51, 53, 55, 74, and 75 were essentially negative by NPD. Such samples would require the use of the alumina column concentration technique to obtain usable NPD patterns. Sample 51, a shallow subsurface sample, shows an unusual FID pattern lacking n-alkane peaks; a behavior very reminiscent of Santa Barbara channel seep samples illustrated in Figure 5 of (4).

Note the unusual appearance of large NPD peaks around an RI value of 2500 in Figures 45, 51, 69, 73, 76, and 77. Their presence in the samples was confirmed by repeated runs, but they are suspected of being contaminants, possibly resulting from unclean or unsuitable containers in which the samples were supplied to us. Again, one must emphasize the need to be alert to sources of contamination when using detectors of such great sensitivity.

CONCLUSIONS FROM THE SURVEY

The similarity of NPD patterns from crudes of common geographical origin would decrease the predicted discriminating ability of the detector in spill cases where several such sources were present. On the other hand, there are fairly distinctive patterns seen among crudes from different sources and even more so from distillate products. Other work in this lab, using samples from the TRIGOM weathering set, indicates that light oils of low viscosity tend to lose their NPD patterns upon weathering. The patterns of heavy residual oils and some heavy crudes appear more stable to weathering, and, since they are also large and distinctive, the NPD appears especially useful for fingerprinting these oils. If N-compounds weather out of light oils by dissolution into the water column, as appears most likely in view of their weight and long t_r's, then perhaps the NPD would be useful in monitoring them in water column studies to assess the effects of chronic oil pollution on the environment. Likewise, the observation of the geographical similarity of the NPD patterns of crudes might yield interesting information in the context of organic geochemistry. Since there is interest (11) in identifying the nitrogen compounds in synthetic oils, they must be subjected to chromatographic and extractive separation and concentration procedures to isolate them for analysis by techniques such as GC-MS. The GC-NPD analysis procedures described here could be useful in keeping track of the nitrogen compound patterns during such complex sample preparation procedures.

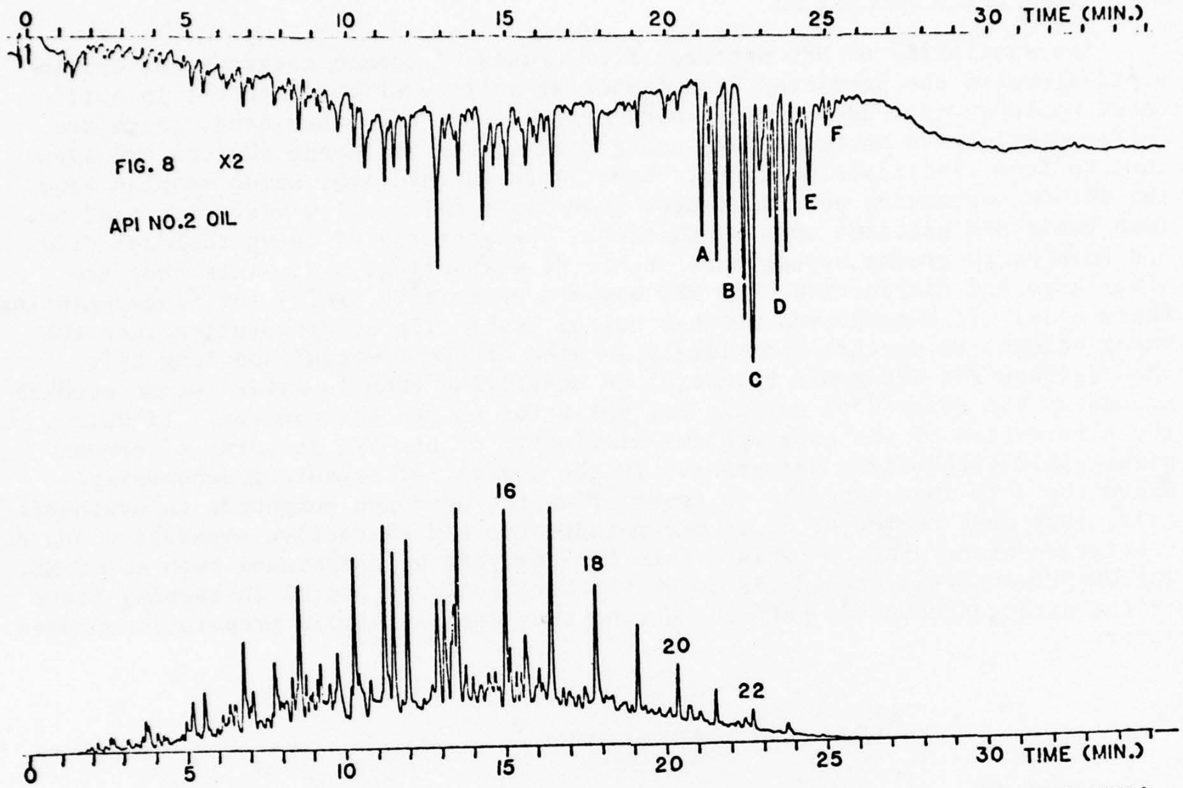


FIG. 8 X2

API NO.2 OIL

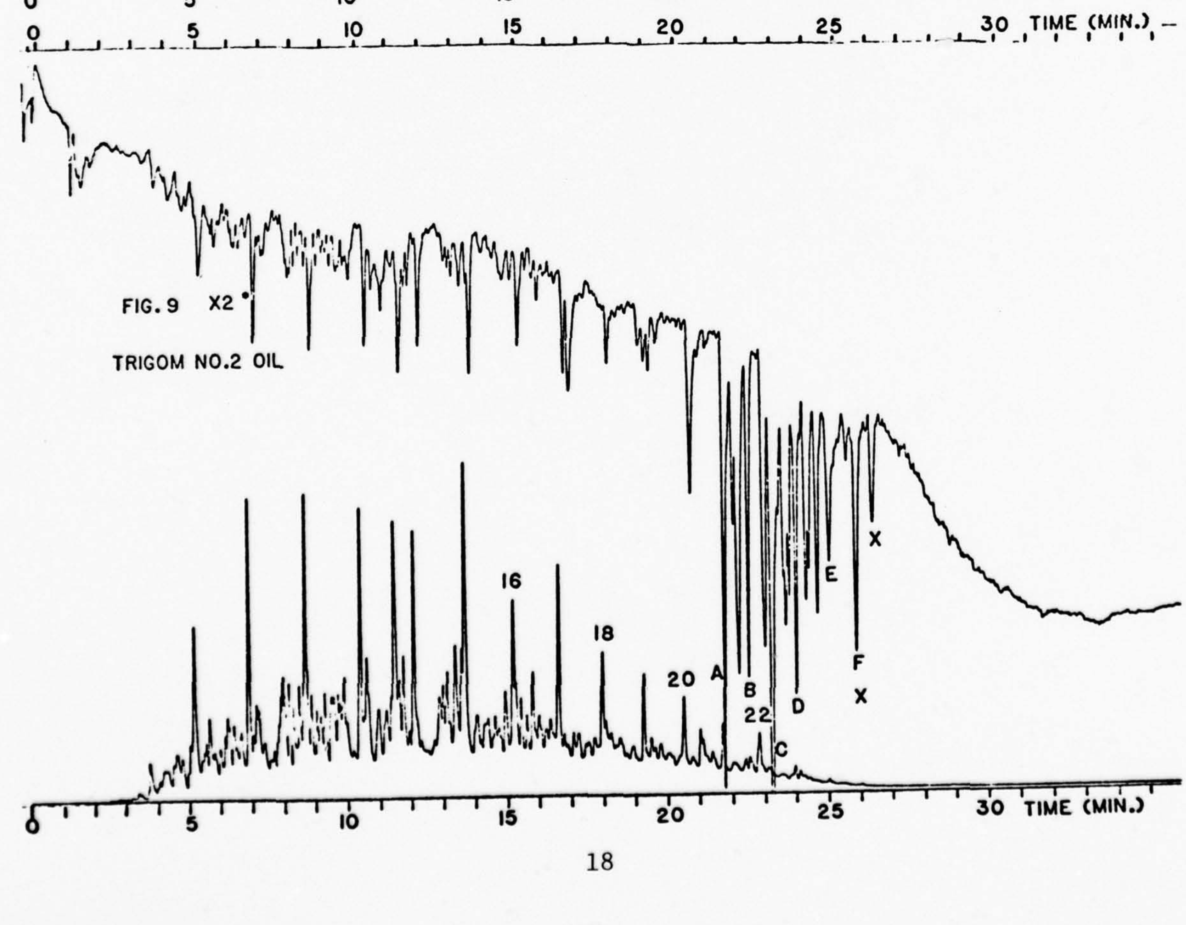


FIG. 9 X2

TRIGOM NO.2 OIL

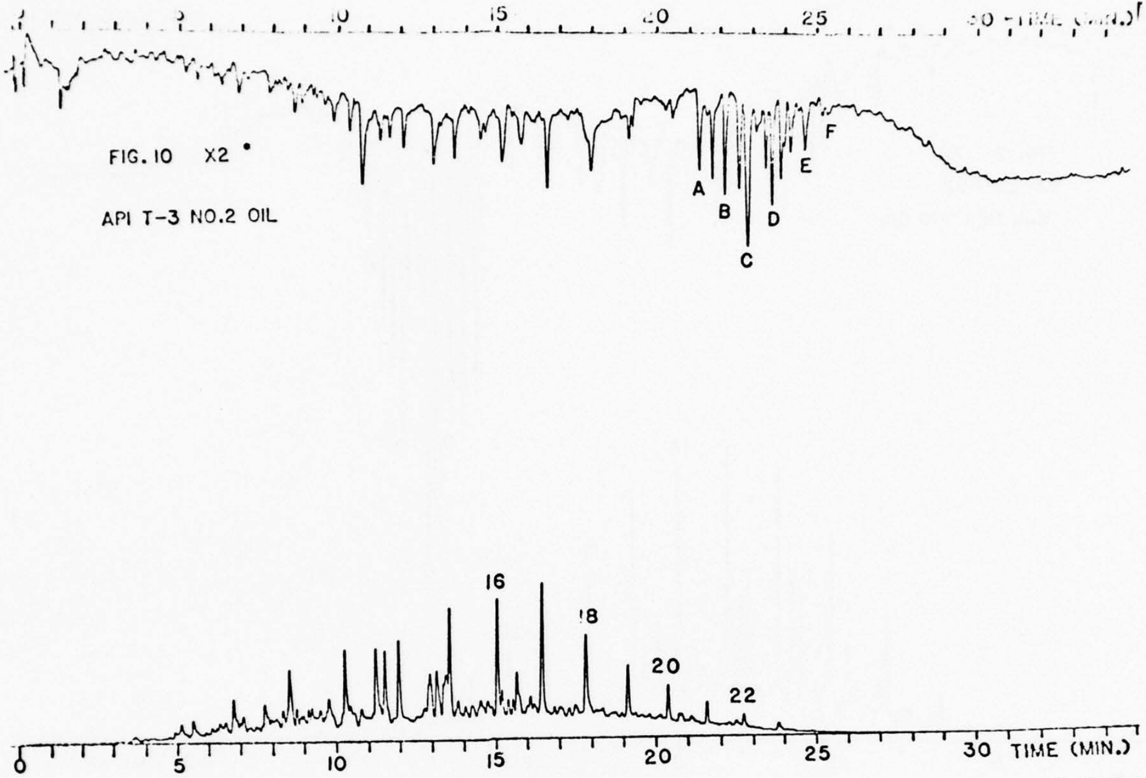


FIG. 10 X2

API T-3 NO.2 OIL

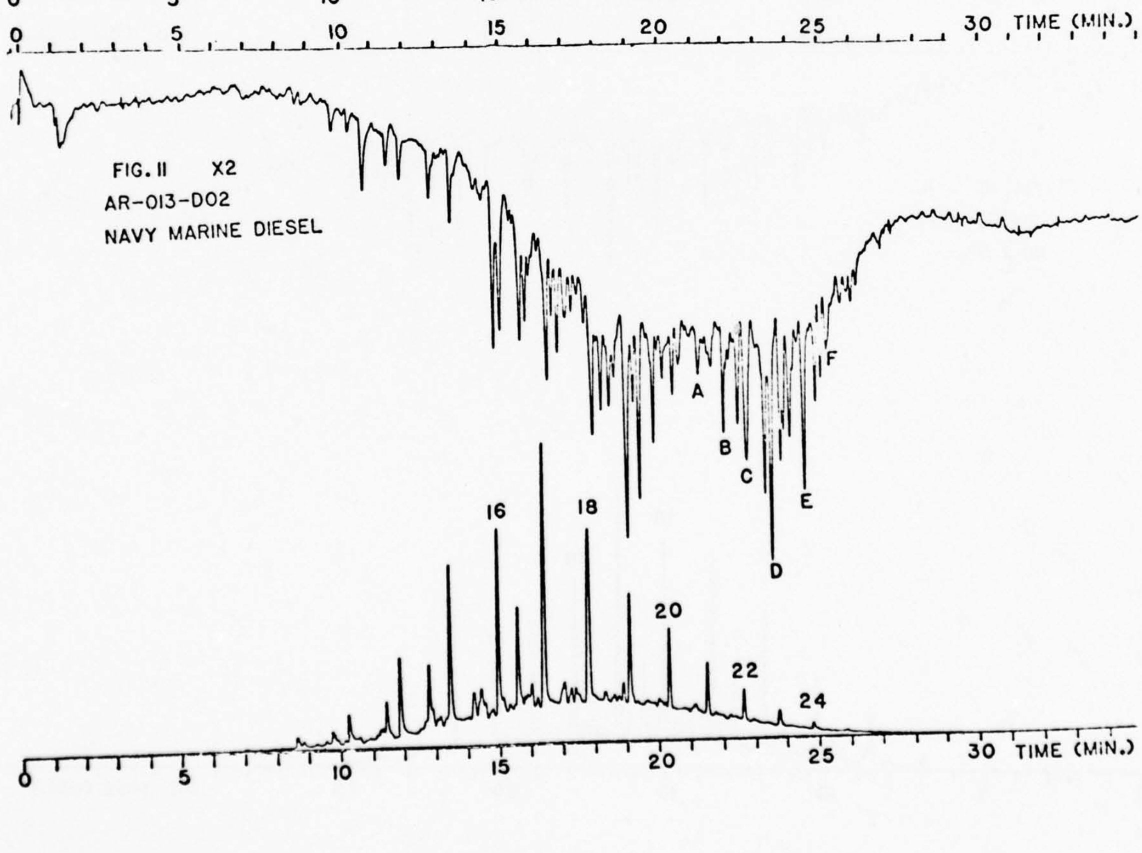


FIG. 11 X2

AR-013-D02

NAVY MARINE DIESEL

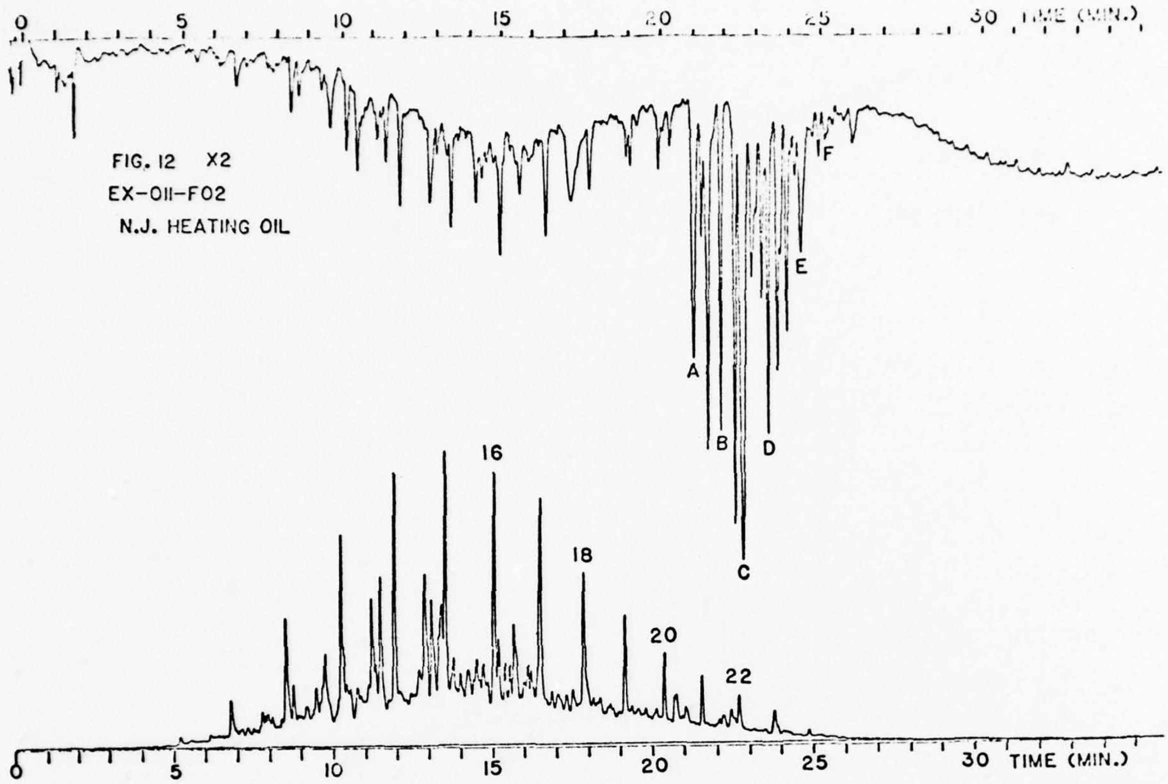


FIG. 12 X2
EX-011-F02
N.J. HEATING OIL

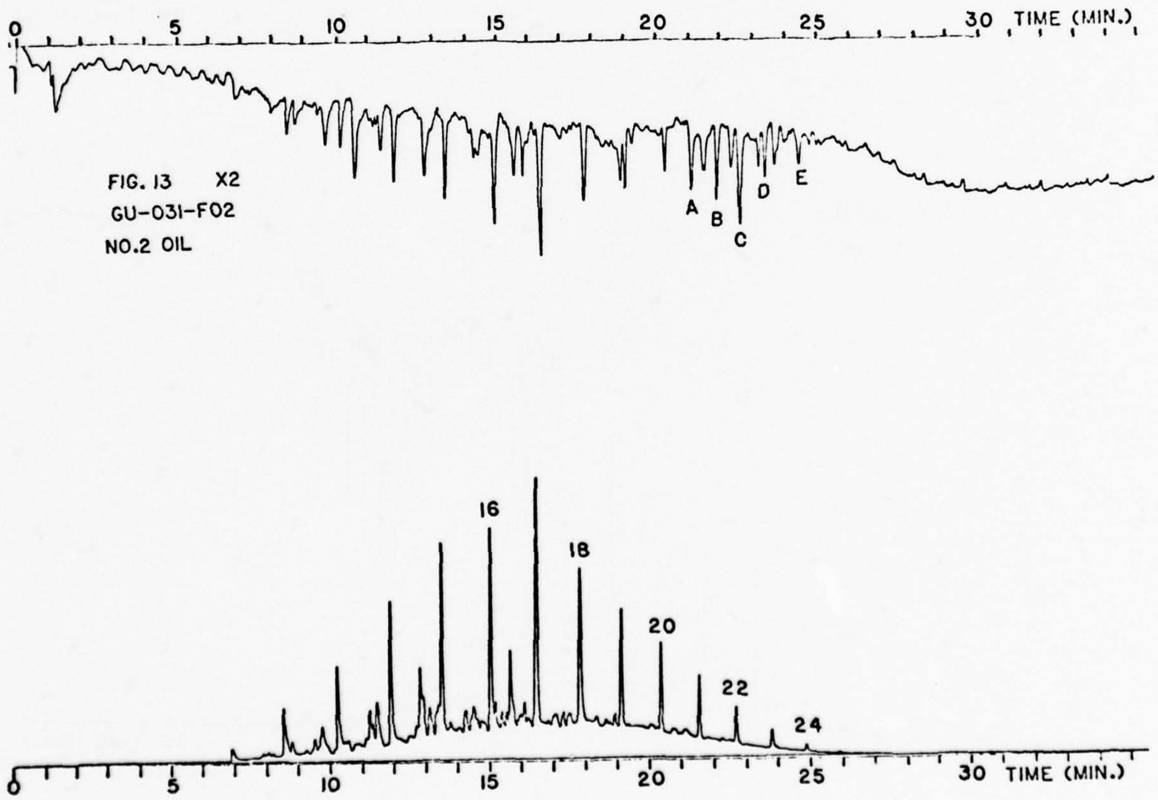


FIG. 13 X2
GU-031-F02
NO.2 OIL

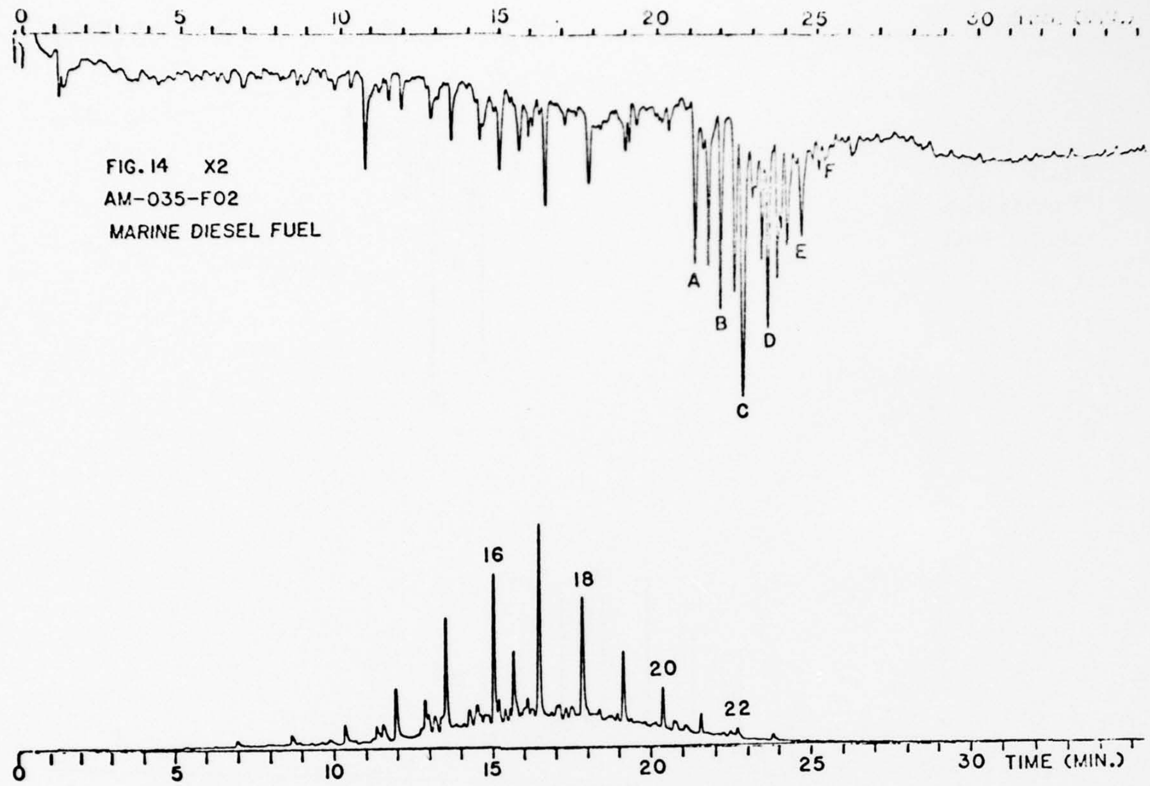


FIG. 14 X2
AM-035-F02
MARINE DIESEL FUEL

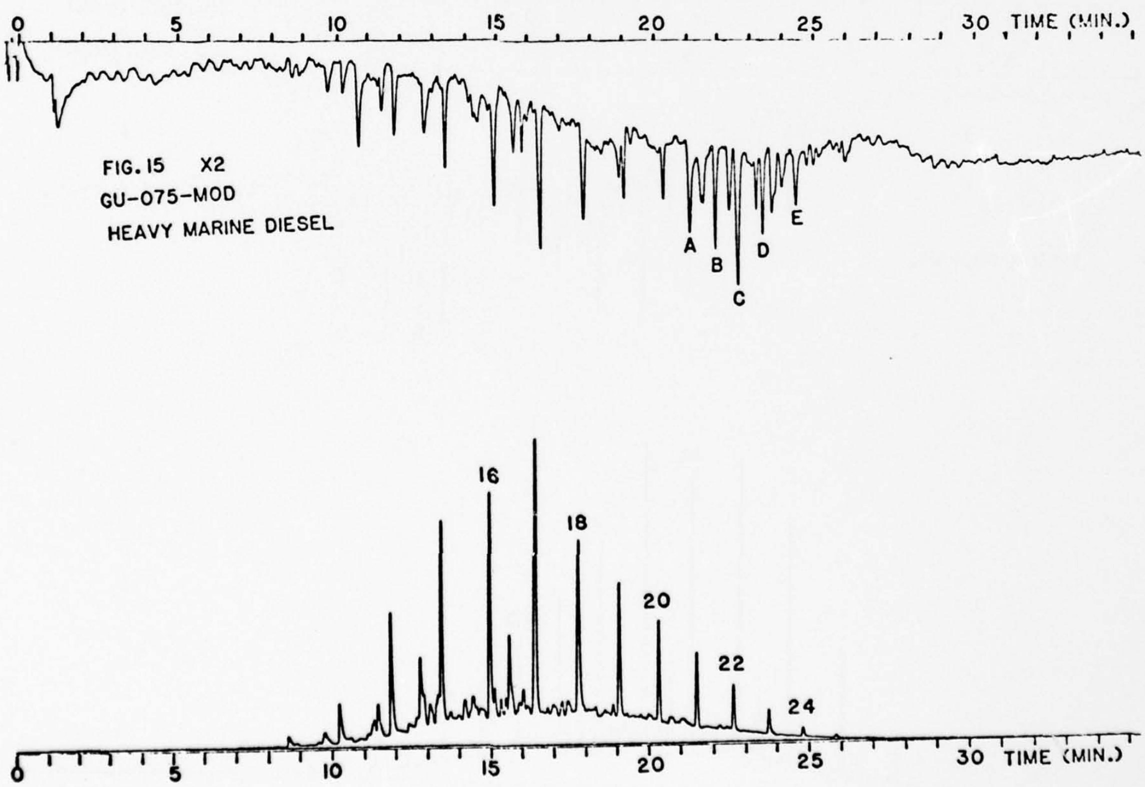


FIG. 15 X2
GU-075-MOD
HEAVY MARINE DIESEL

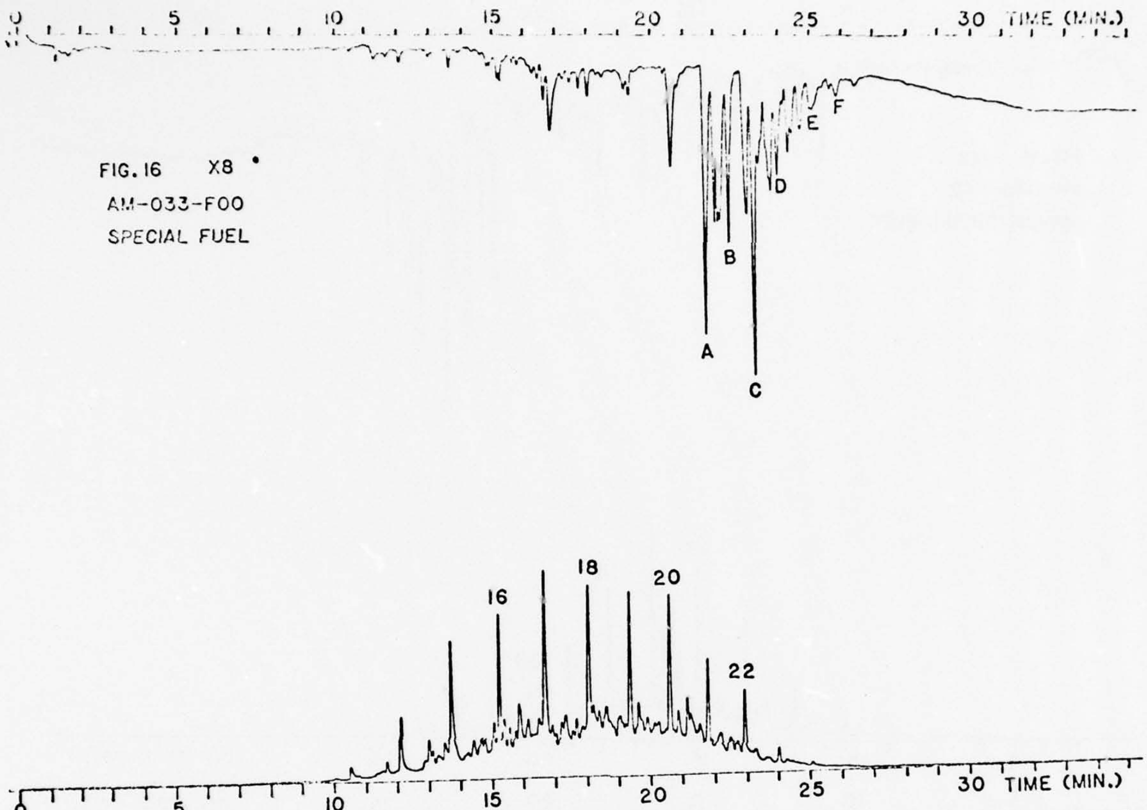


FIG. 16 X8
AM-033-F00
SPECIAL FUEL

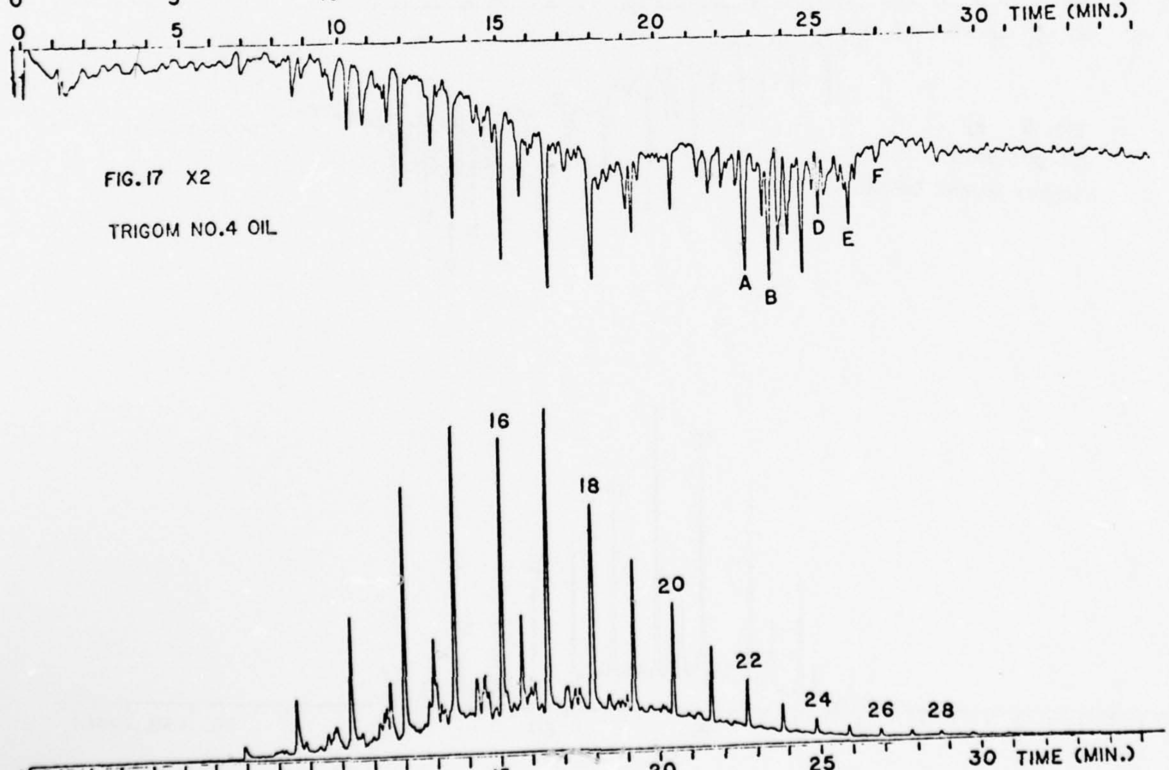
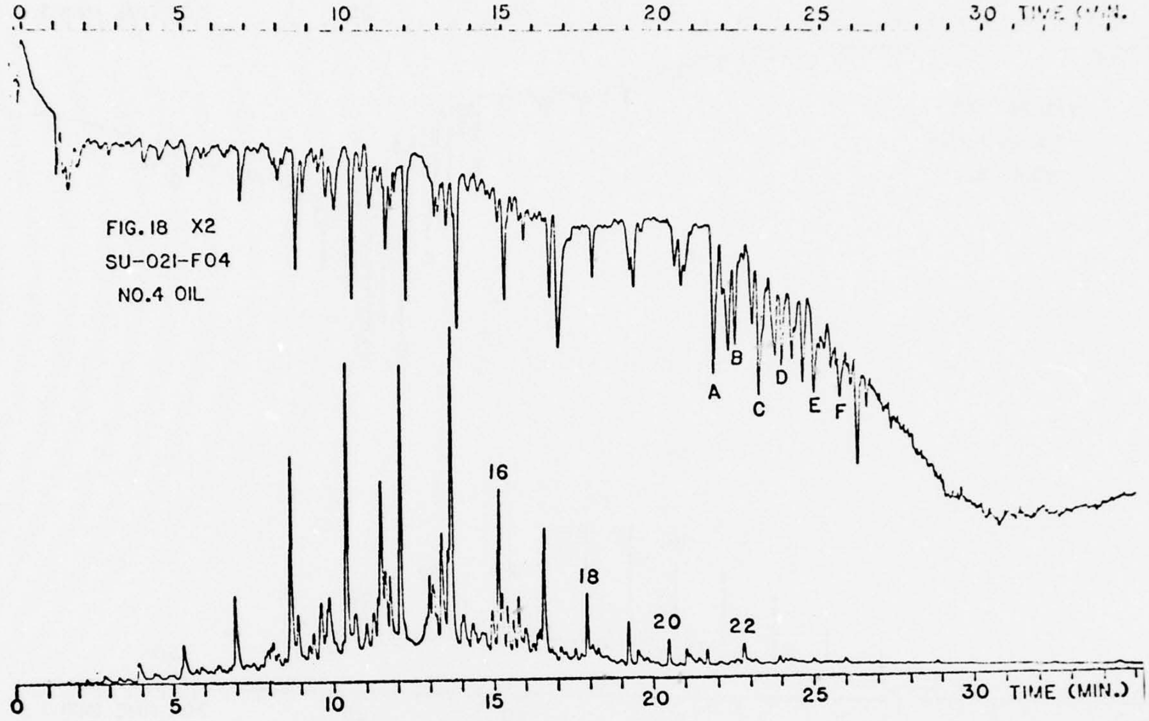
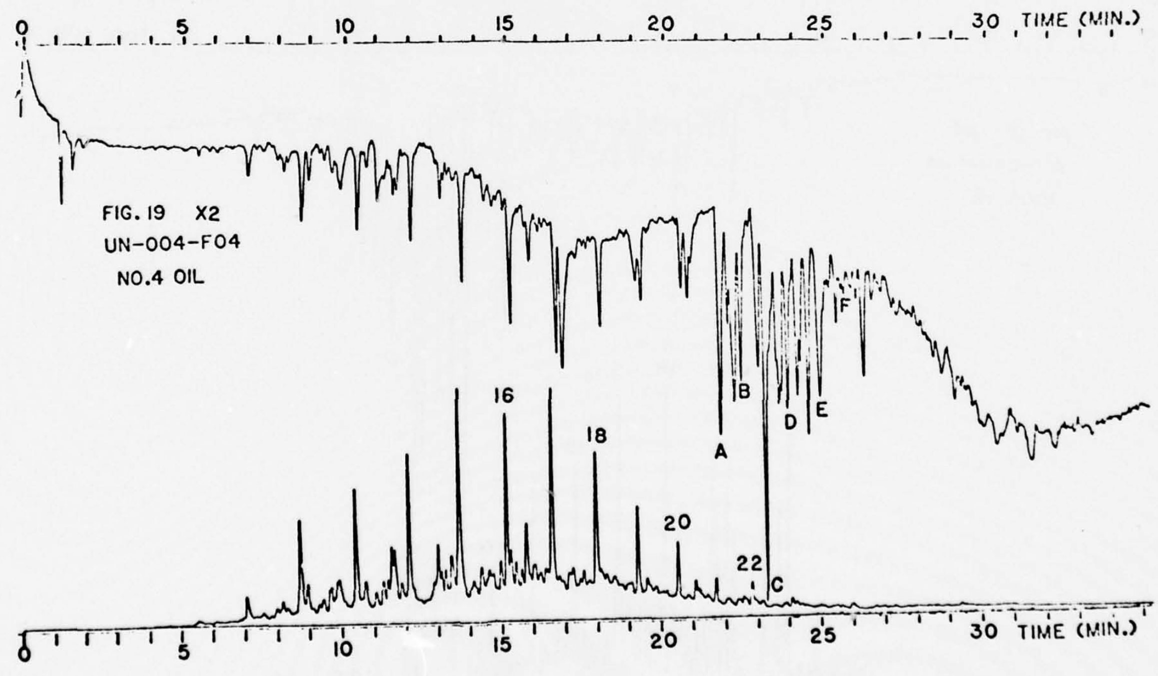


FIG. 17 X2
TRIGOM NO.4 OIL


0
5
10
15
20
25
30
TIME (MIN.)
FIG. 18 X2
SU-021-F04
NO.4 OIL
A
B
C
D
E
F
16
18
20
22


0
5
10
15
20
25
30
TIME (MIN.)
FIG. 19 X2
UN-004-F04
NO.4 OIL
A
B
C
D
E
F
16
18
20
22

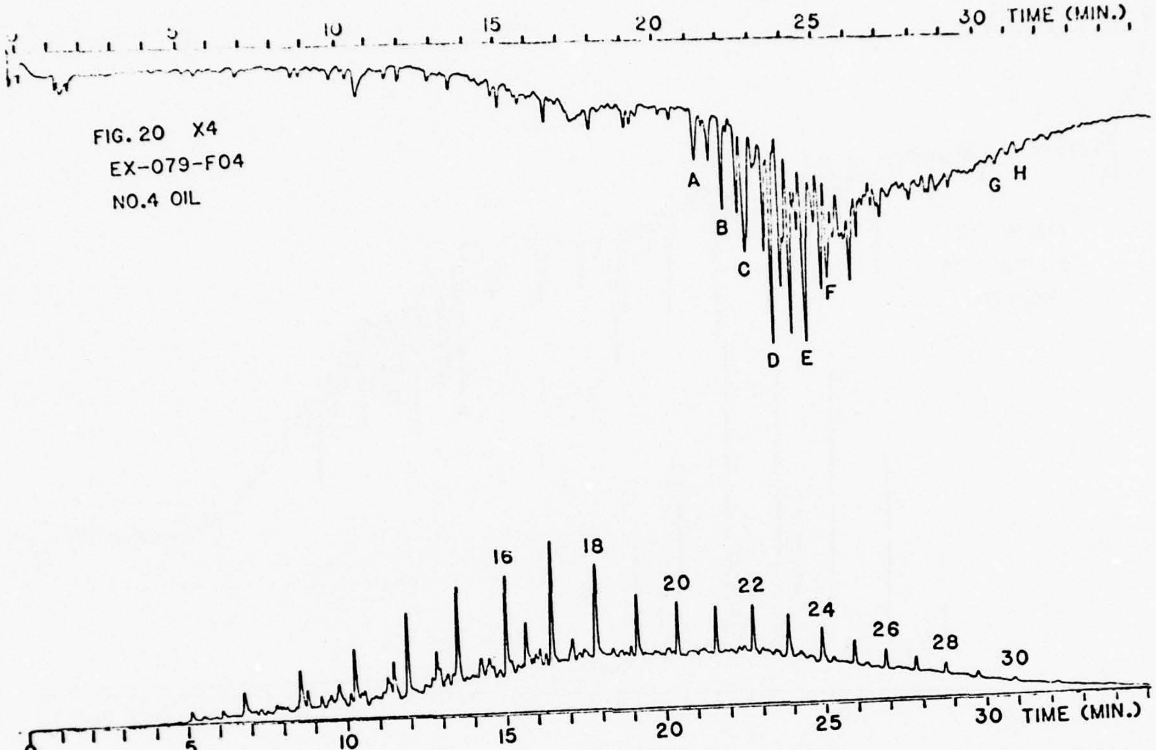


FIG. 20 X4
EX-079-F04
NO.4 OIL

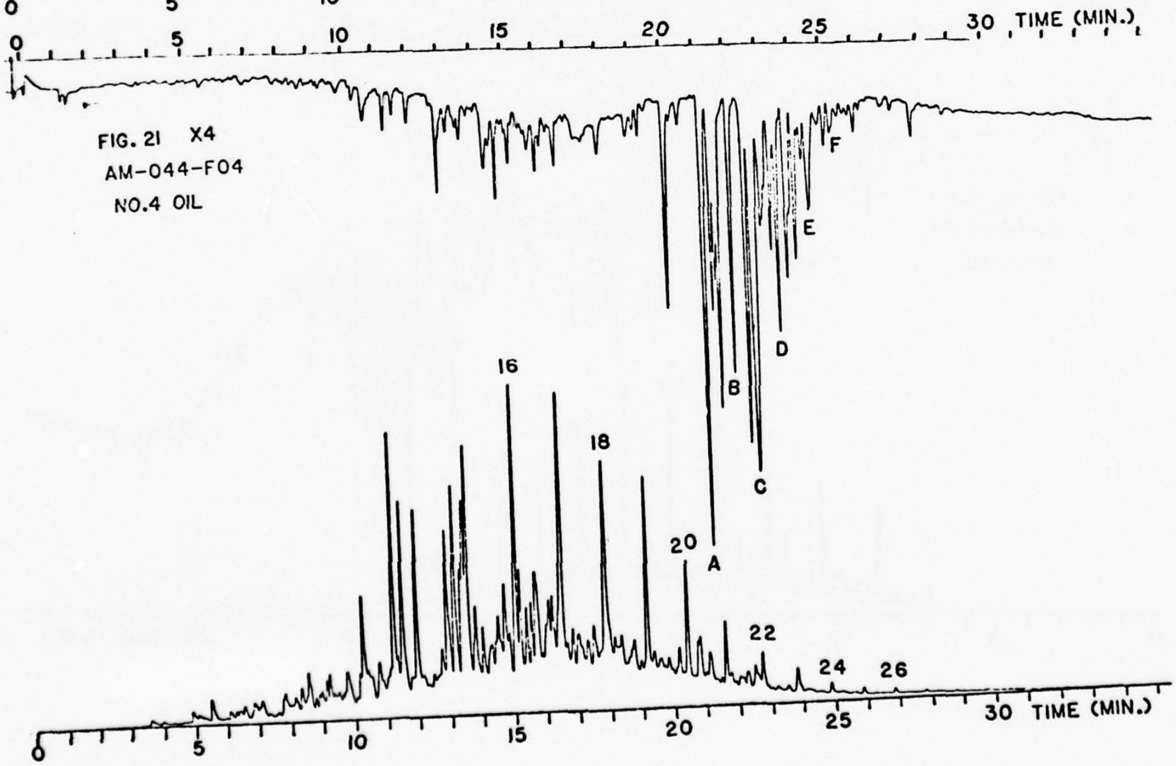


FIG. 21 X4
AM-044-F04
NO.4 OIL

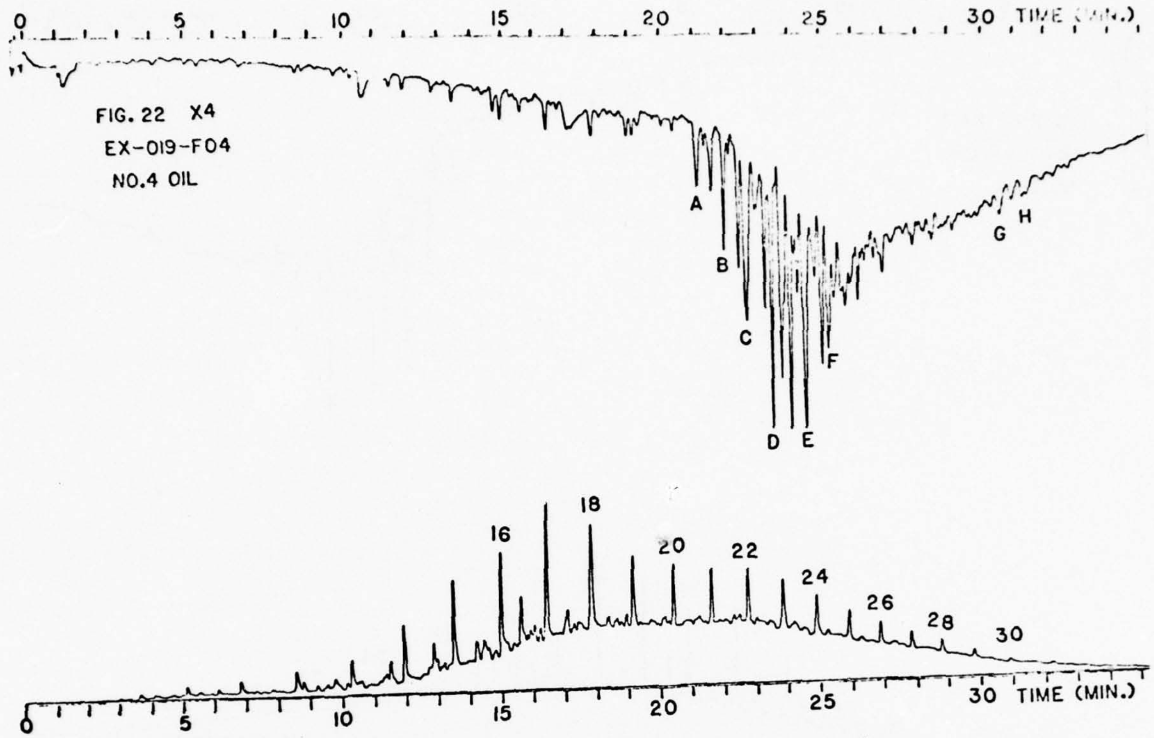


FIG. 22 X4
EX-019-F04
NO.4 OIL
A
B
C
D
E
F
G
H
16
18
20
22
24
26
28
30
TIME (MIN.)
0
5
10
15
20
25
30

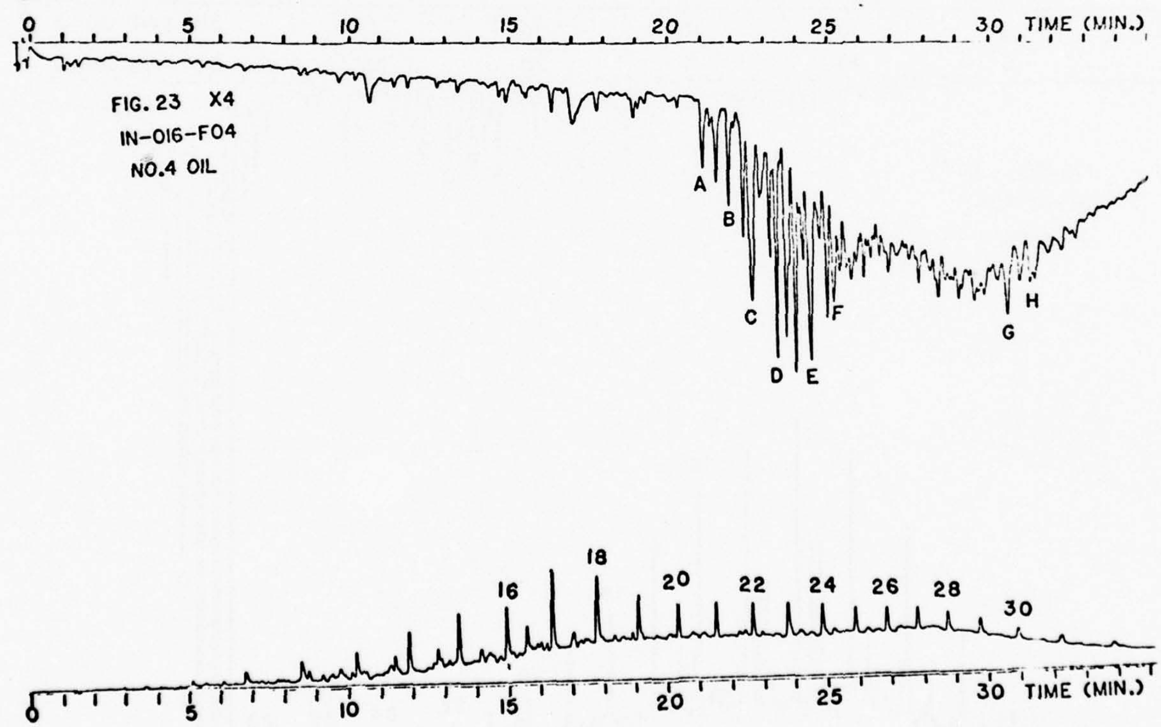


FIG. 23 X4
IN-016-F04
NO.4 OIL
A
B
C
D
E
F
G
H
16
18
20
22
24
26
28
30
TIME (MIN.)
0
5
10
15
20
25
30

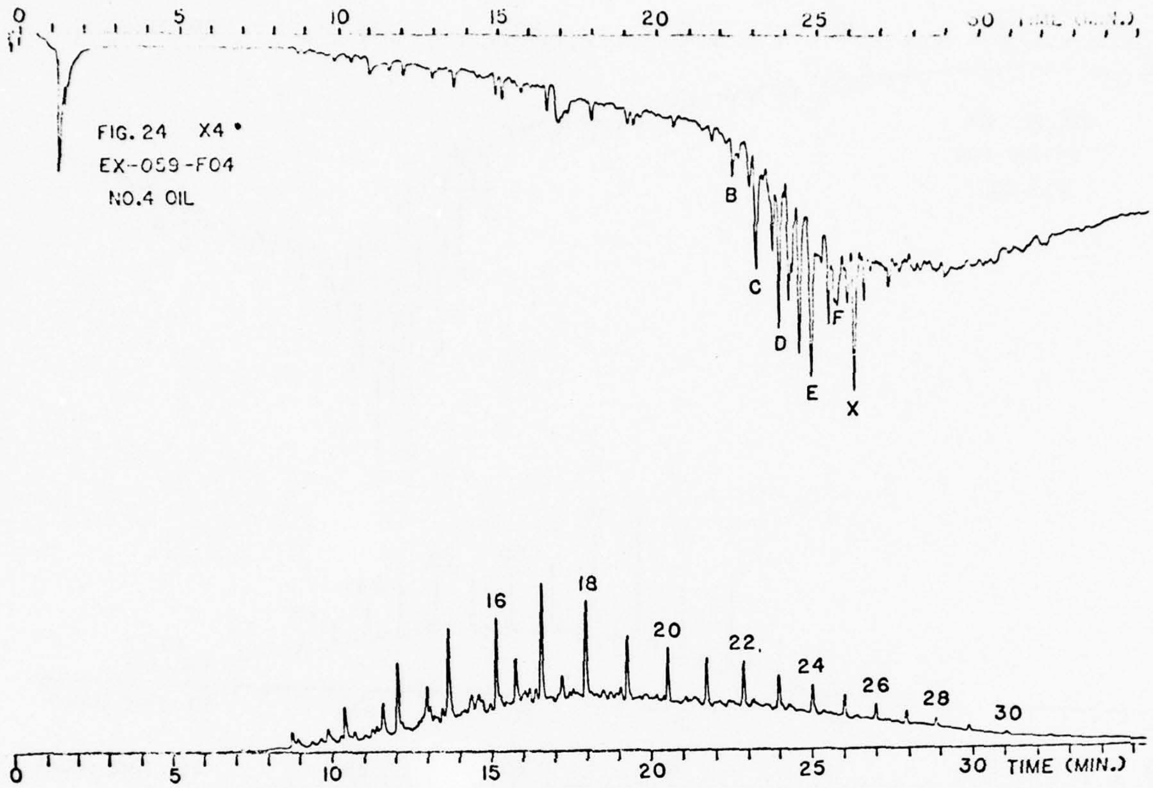


FIG. 24 X4 •
EX-059-F04
NO.4 OIL

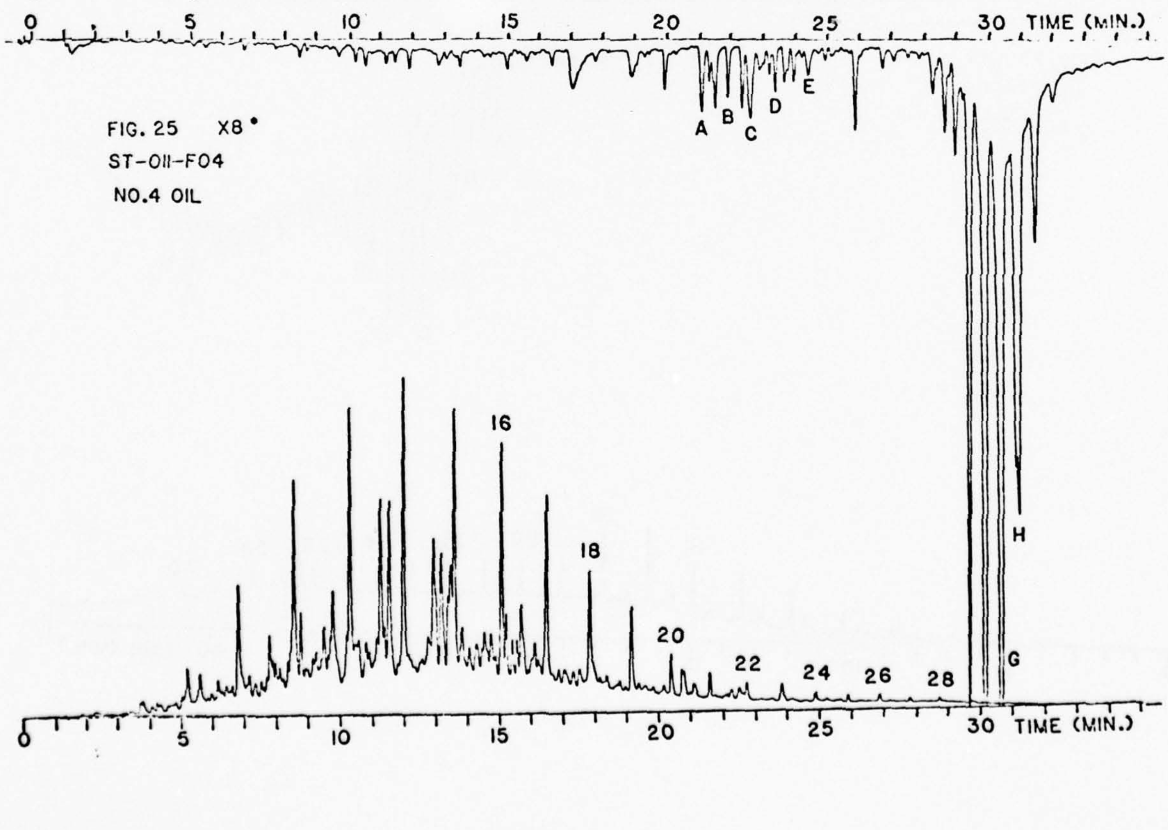


FIG. 25 X8 •
ST-011-F04
NO.4 OIL

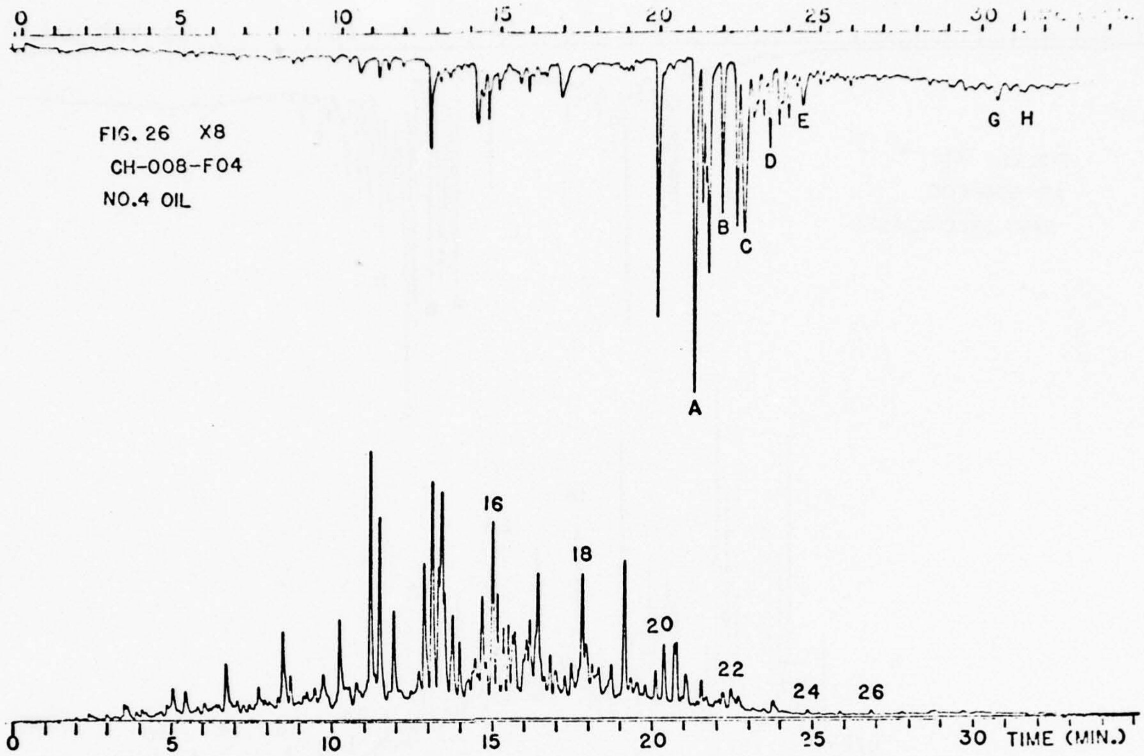


FIG. 26 X8
CH-008-F04
NO.4 OIL

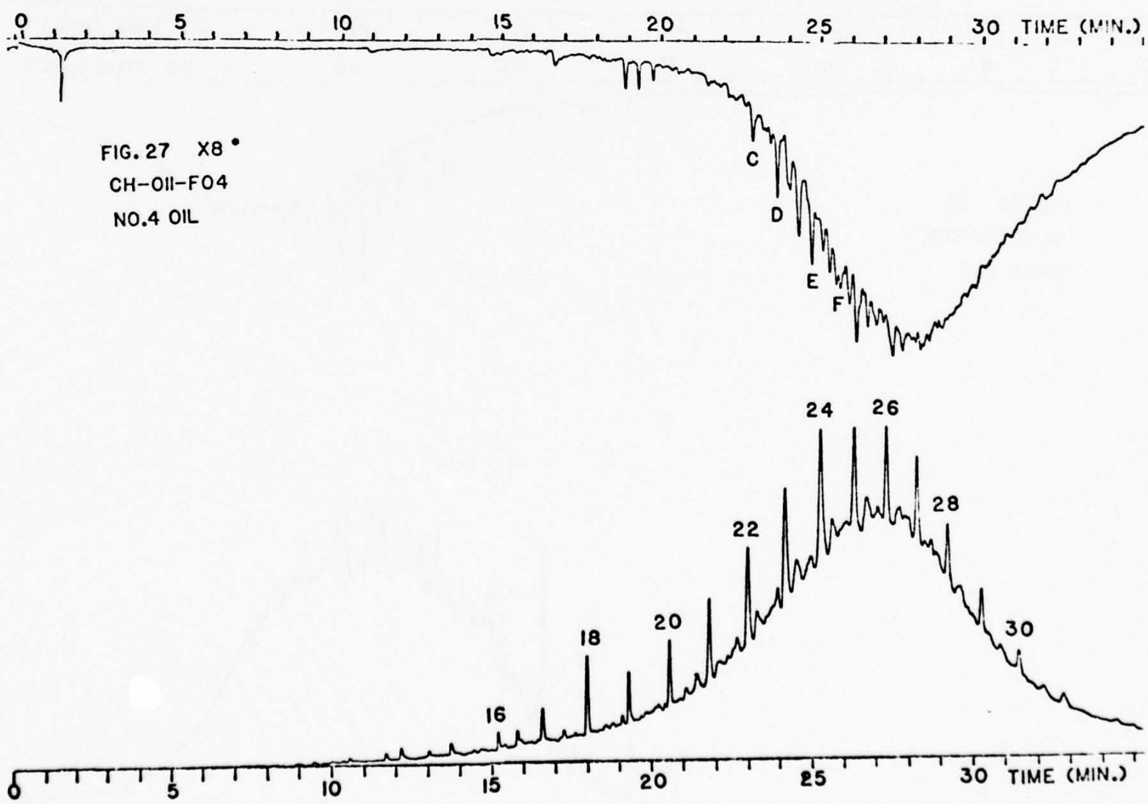


FIG. 27 X8
CH-011-F04
NO.4 OIL

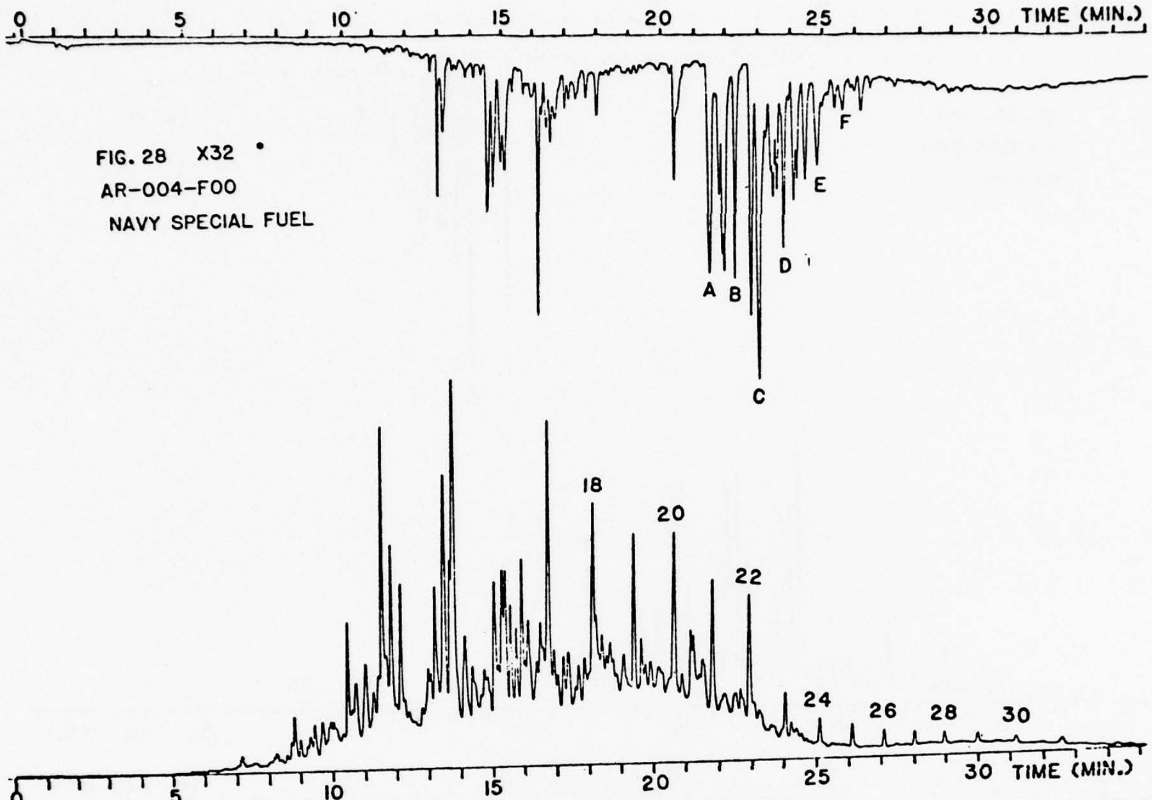


FIG. 28 X32
AR-004-F00
NAVY SPECIAL FUEL

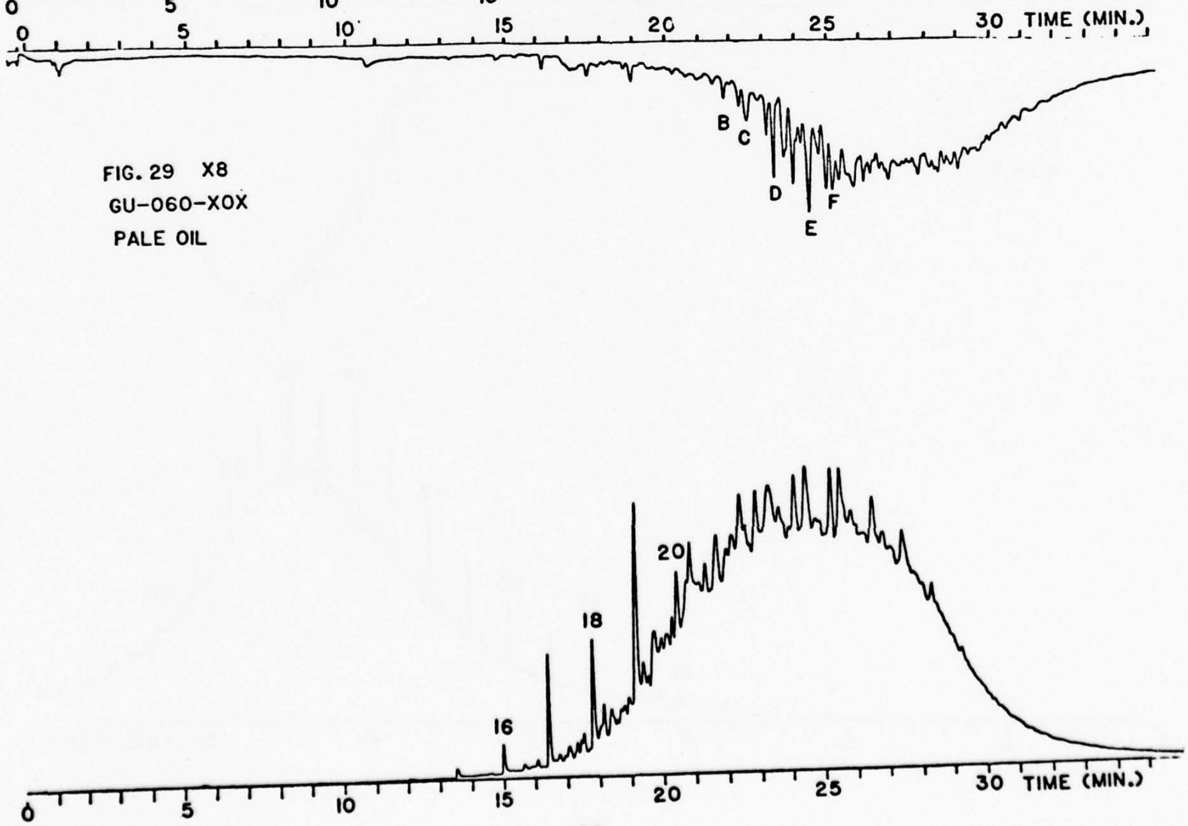


FIG. 29 X8
GU-060-XOX
PALE OIL

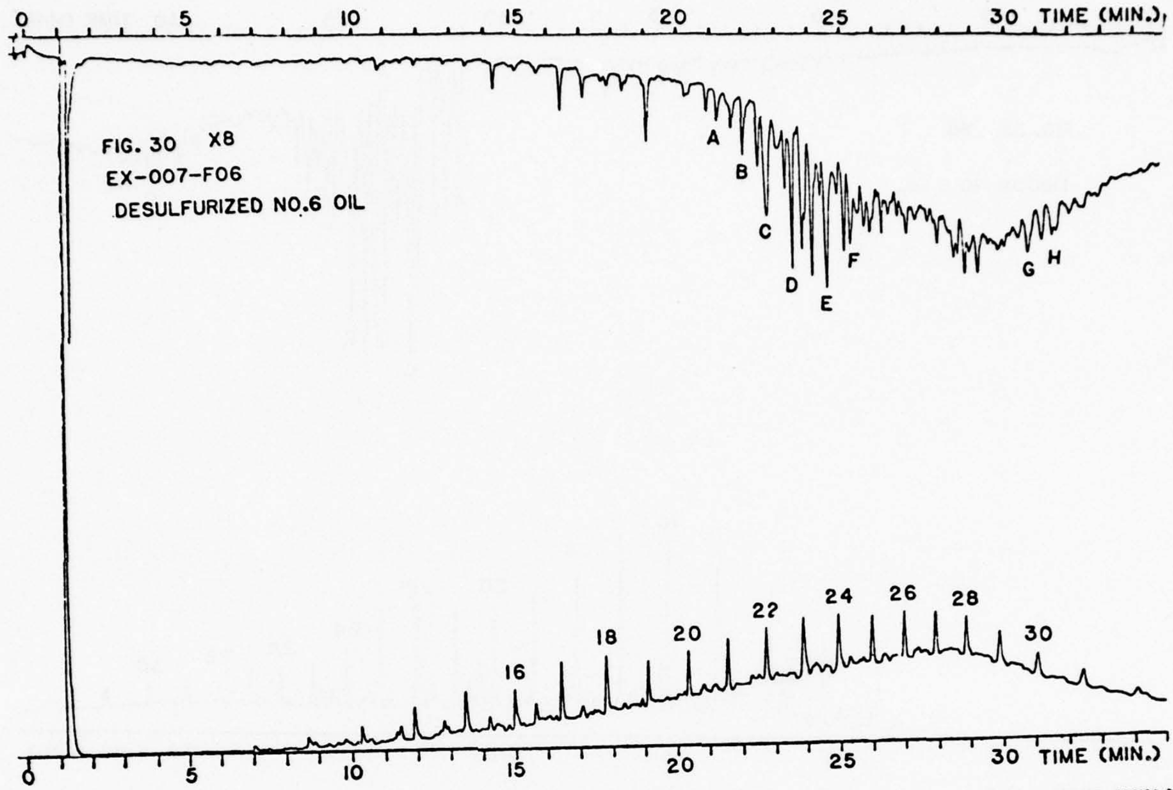


FIG. 30 X8
EX-007-F06
DESULFURIZED NO.6 OIL

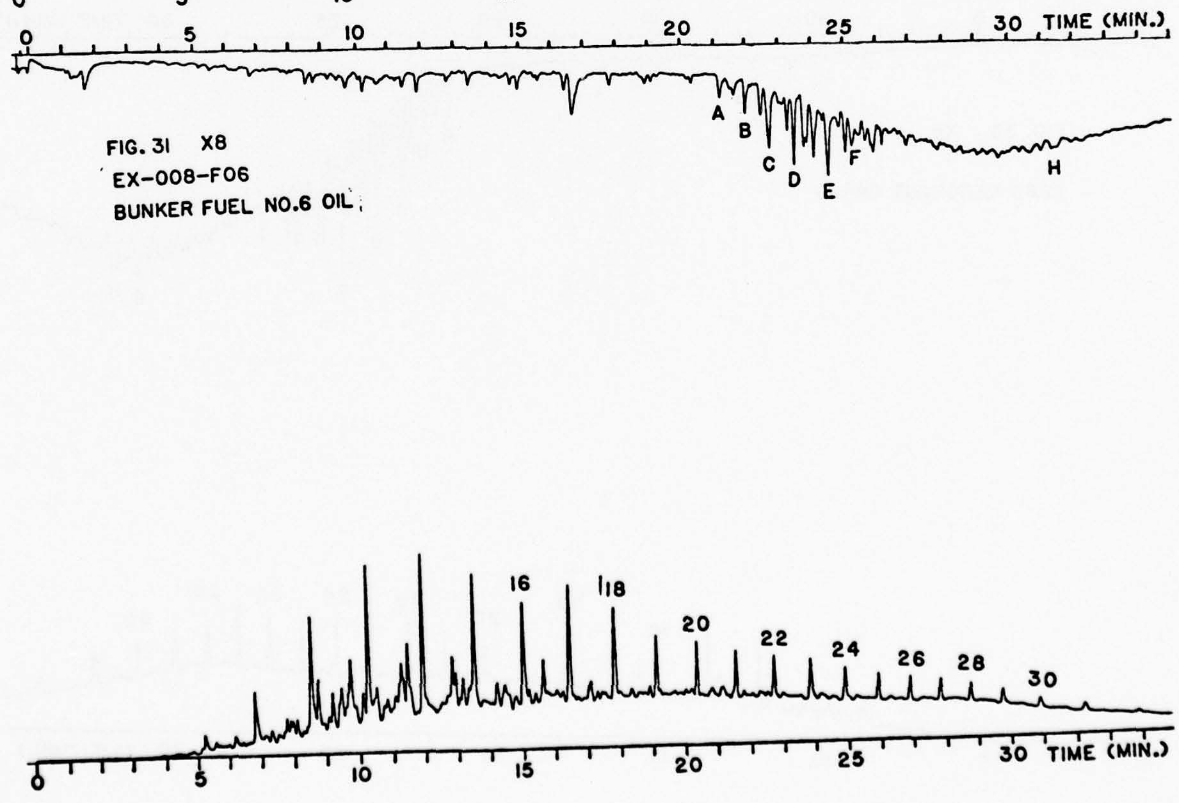


FIG. 31 X8
EX-008-F06
BUNKER FUEL NO.6 OIL

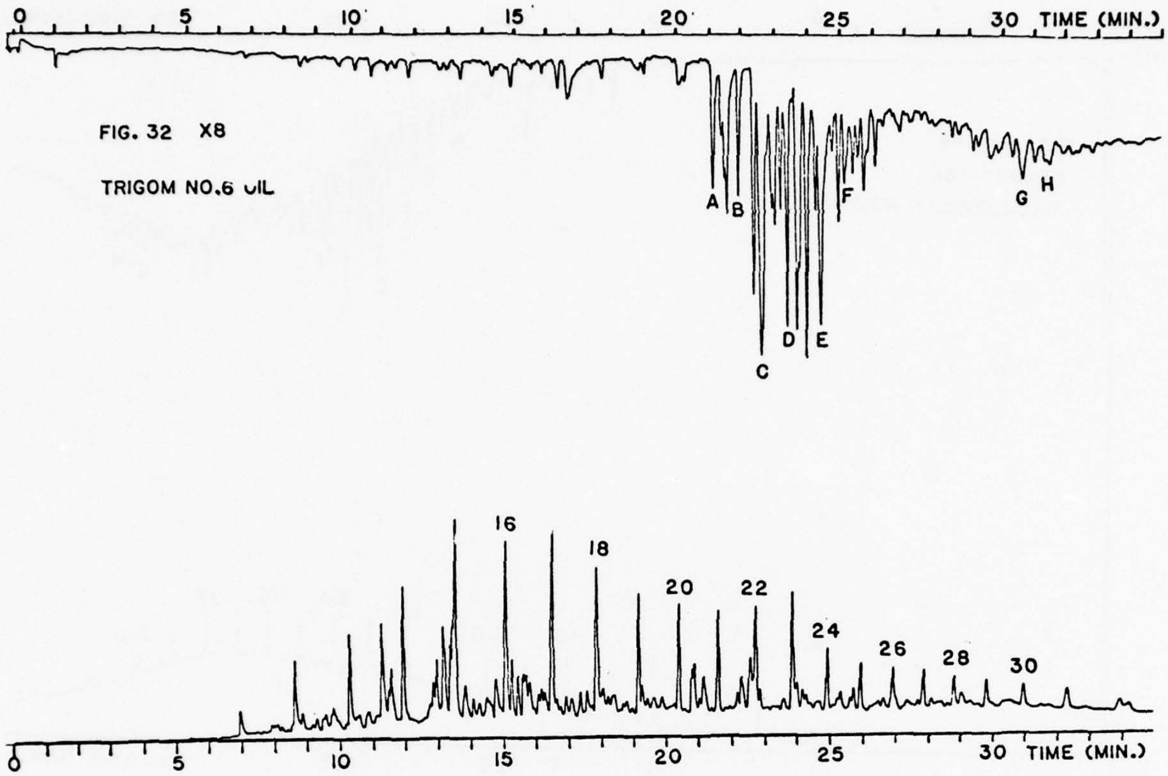


FIG. 32 X8

TRIGOM NO.6 OIL

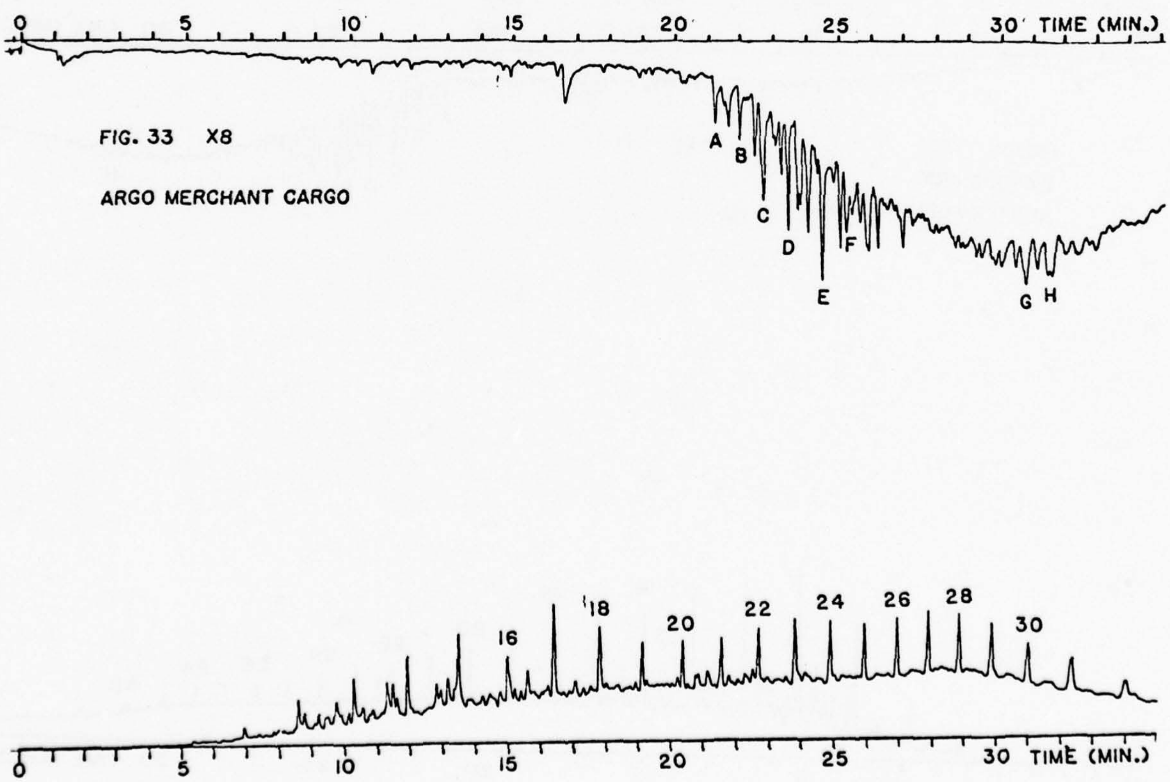


FIG. 33 X8

ARGO MERCHANT CARGO

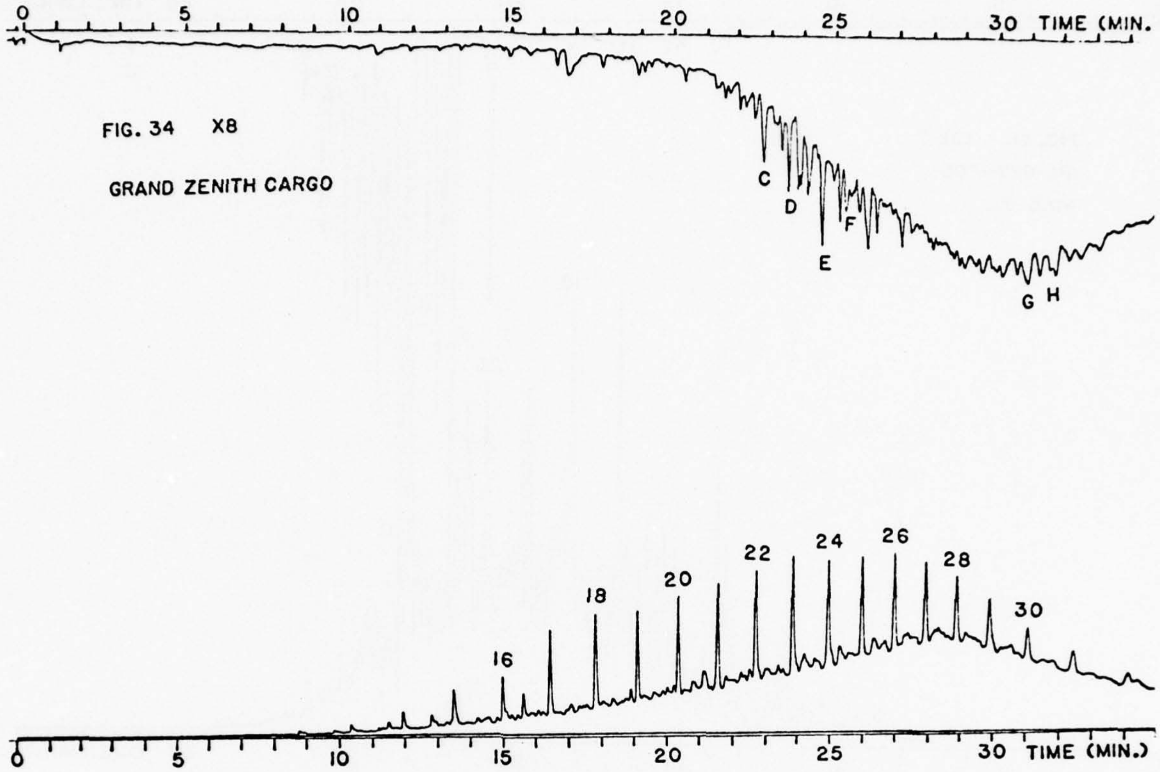


FIG. 34 X8

GRAND ZENITH CARGO

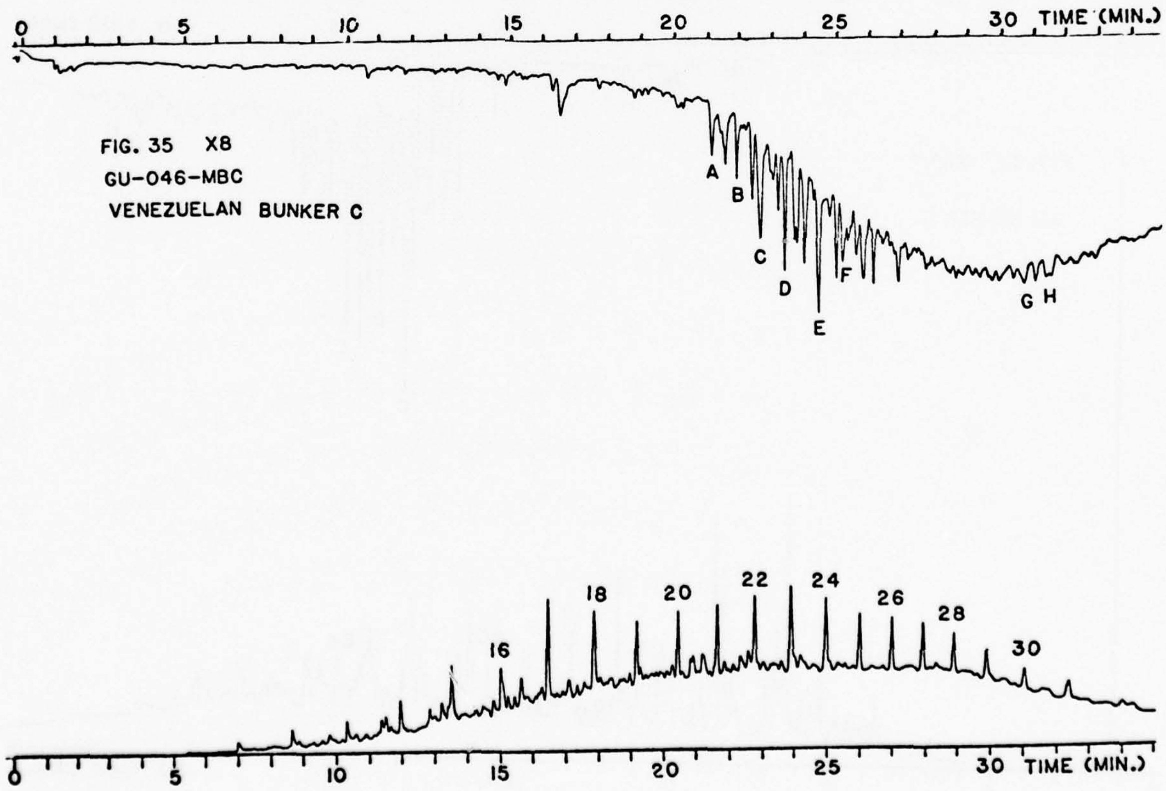


FIG. 35 X8

GU-046-MBC

VENEZUELAN BUNKER C

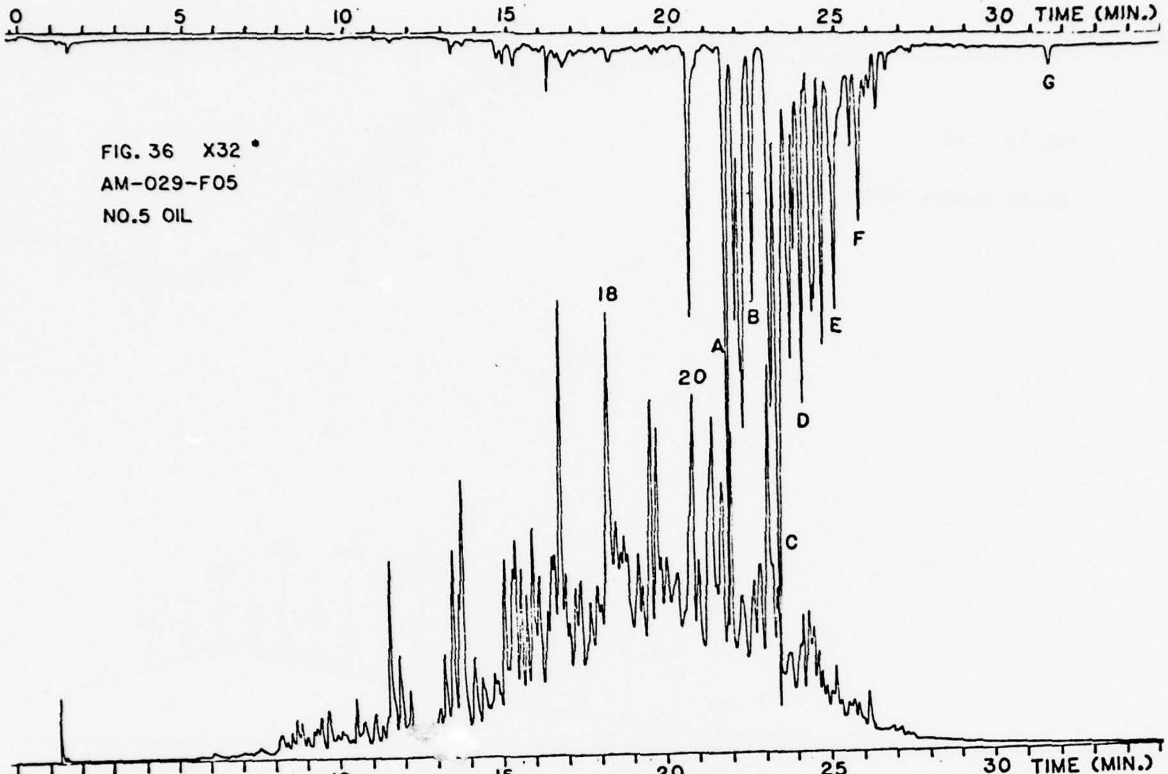


FIG. 36 X32 •
AM-029-F05
NO.5 OIL
TIME (MIN.)
18
20
A
B
C
D
E
F
G

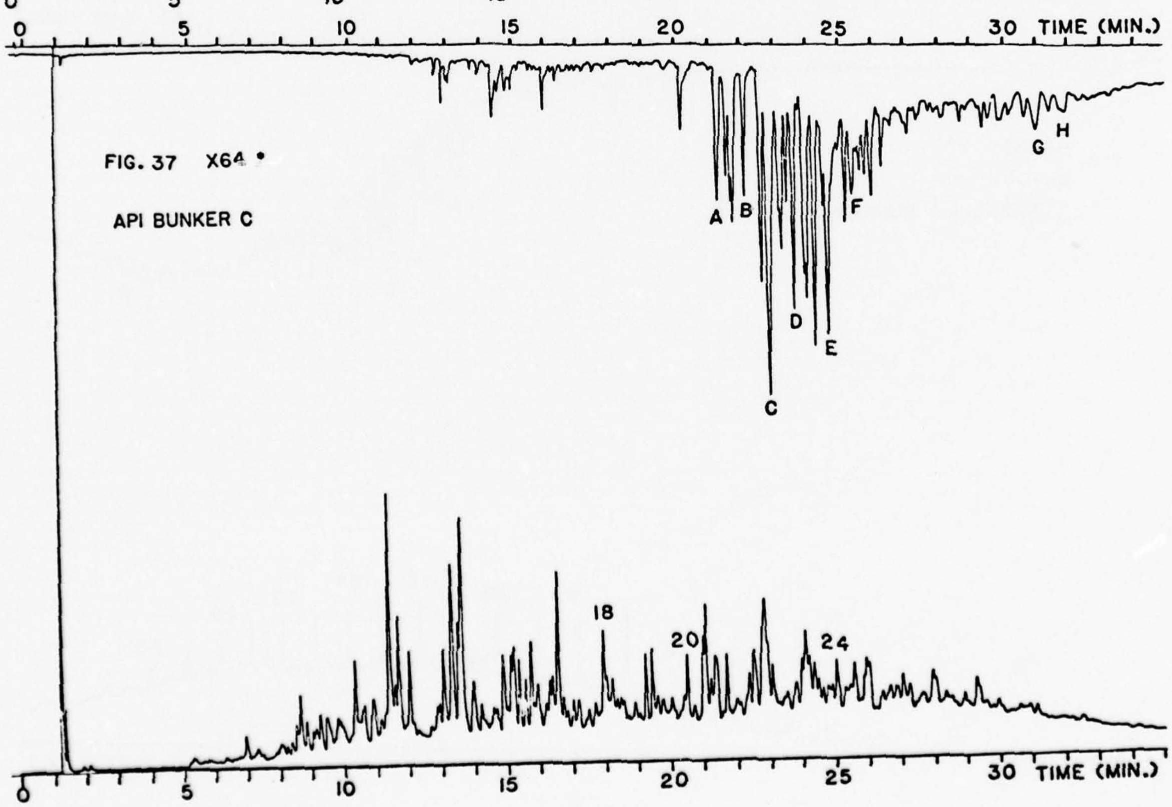


FIG. 37 X64 •
API BUNKER C
TIME (MIN.)
A
B
C
D
E
F
G
H
18
20
24

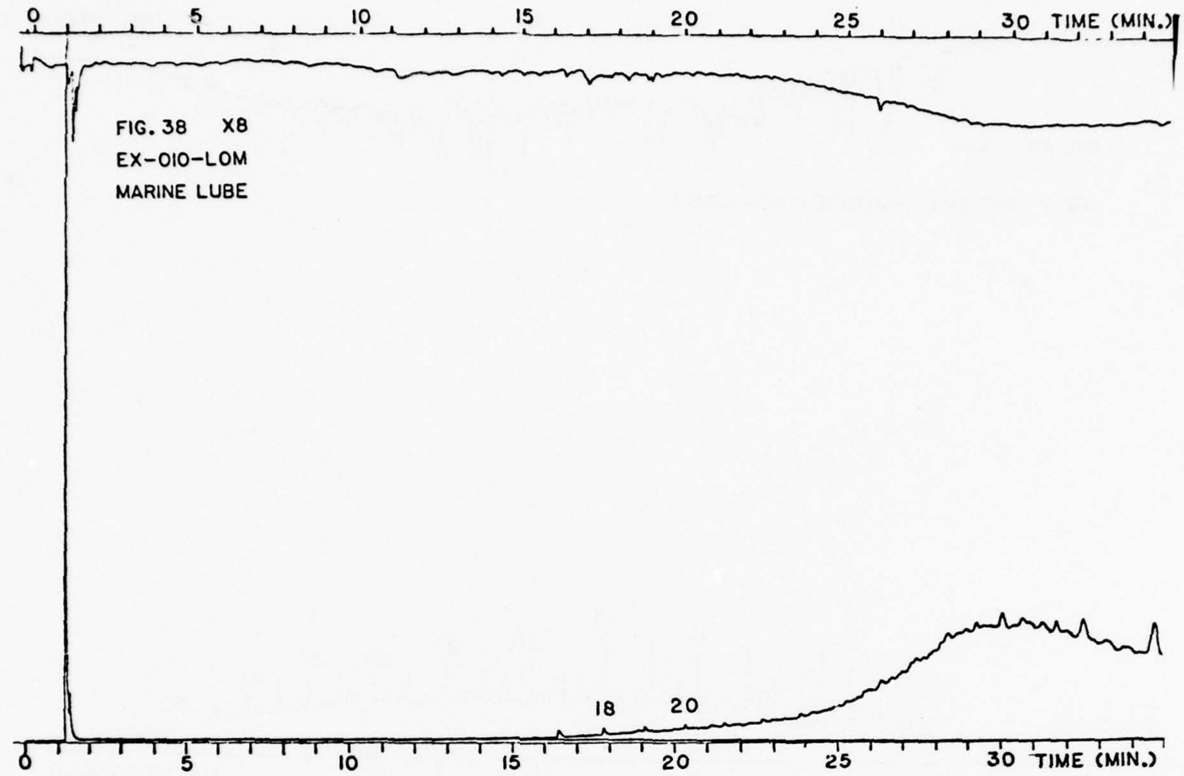


FIG. 38 X8
EX-010-LOM
MARINE LUBE

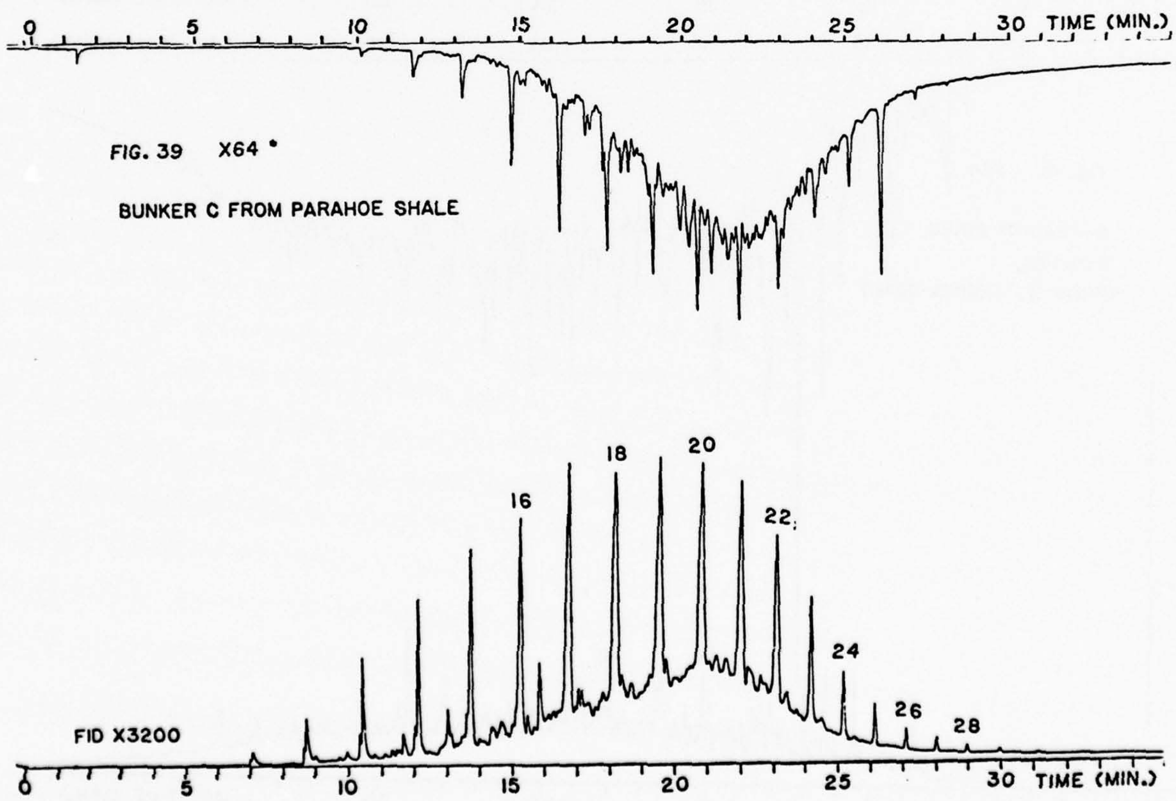


FIG. 39 X64 *

BUNKER C FROM PARAHOE SHALE

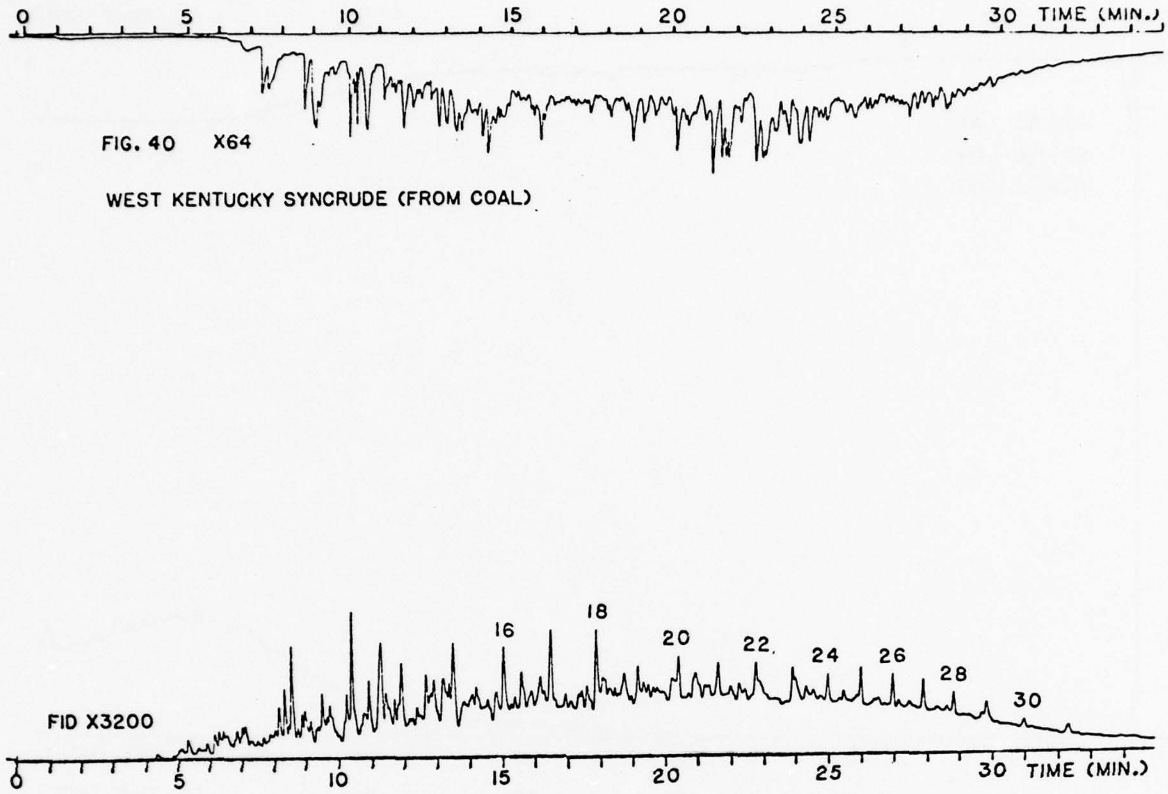


FIG. 40 X64

WEST KENTUCKY SYNCRUDE (FROM COAL)

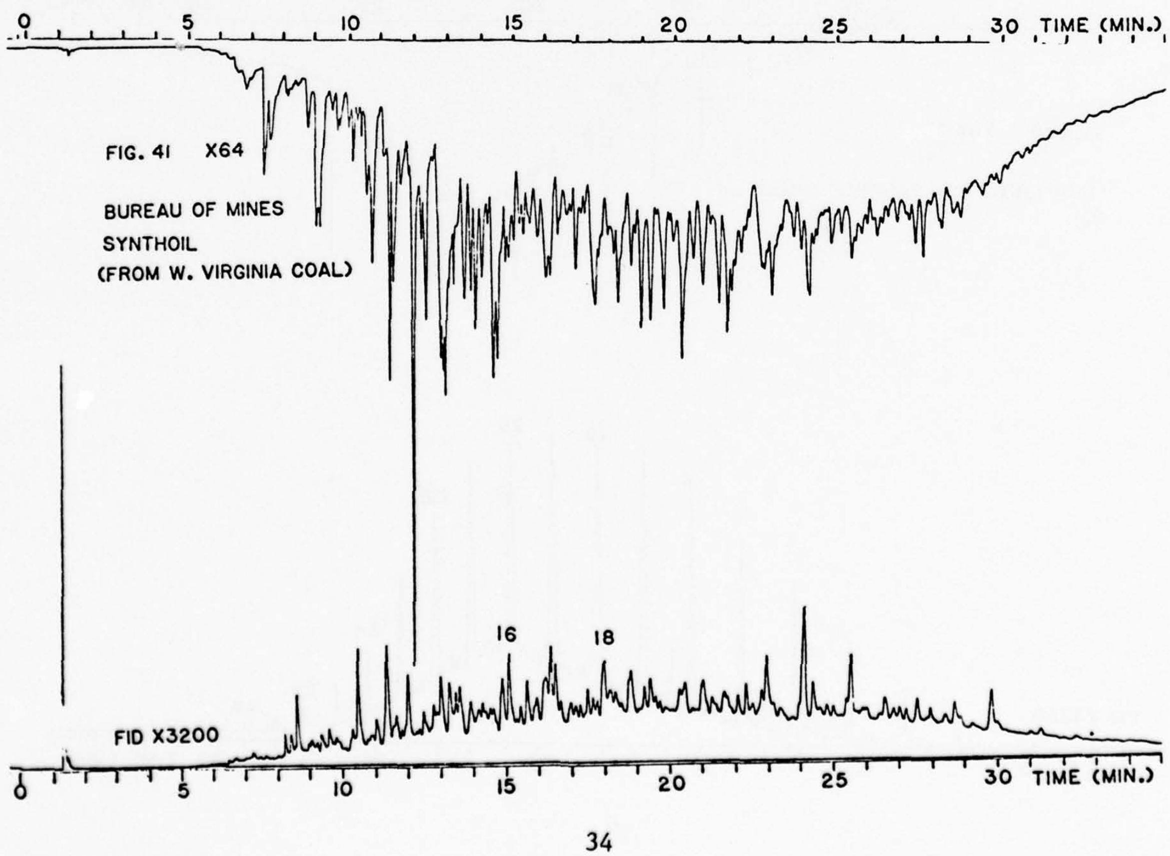


FIG. 41 X64

BUREAU OF MINES
SYNTHOIL
(FROM W. VIRGINIA COAL)

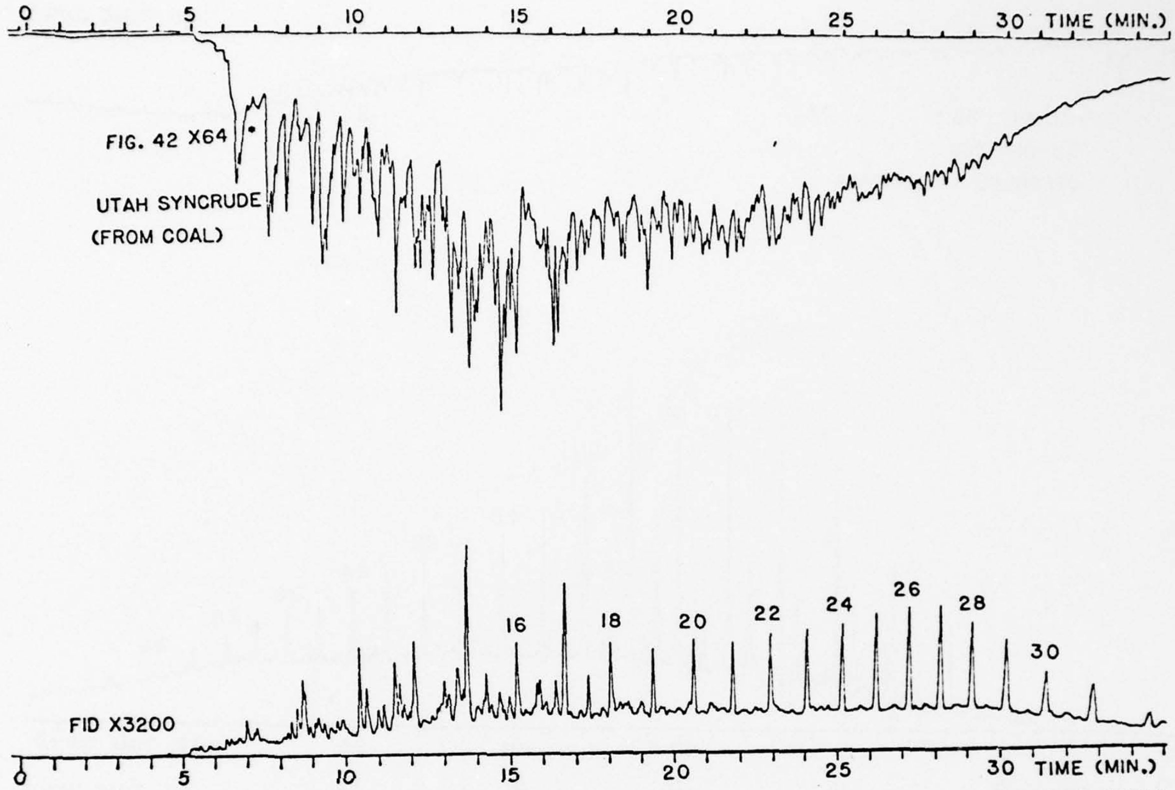


FIG. 42 X64

UTAH SYNCRUDE (FROM COAL)

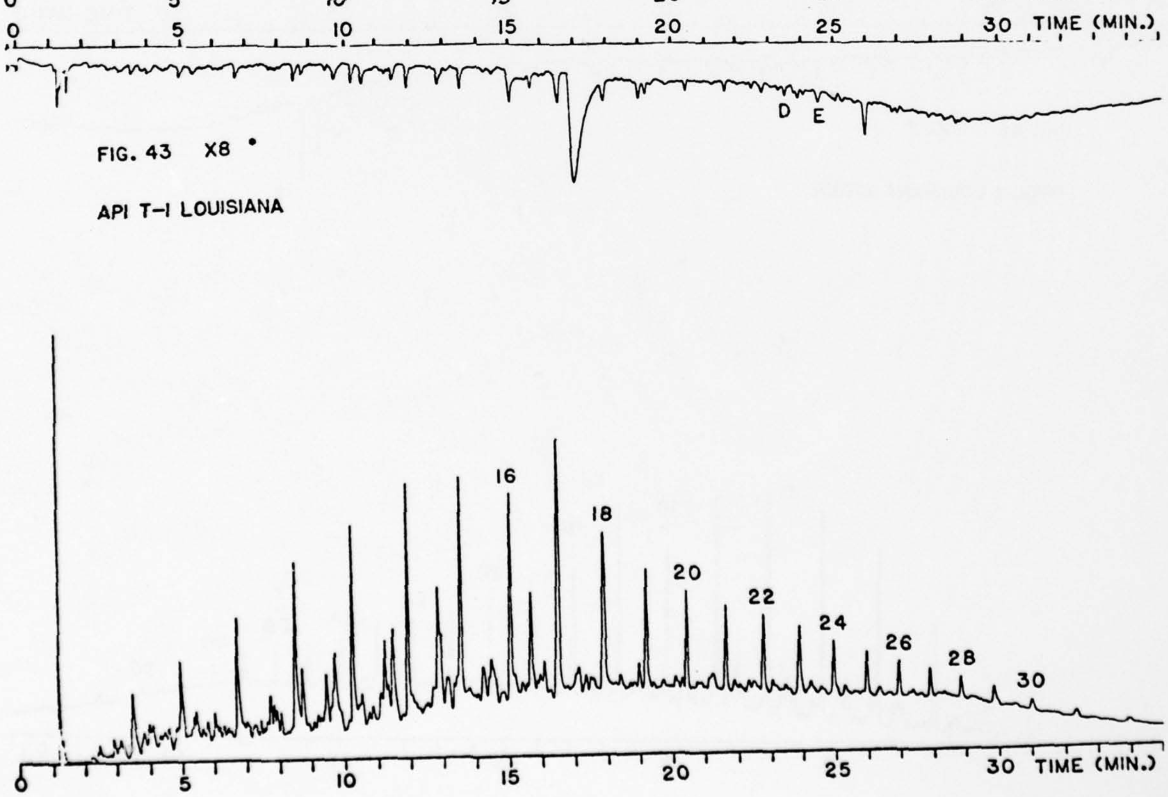


FIG. 43 X8

API T-1 LOUISIANA

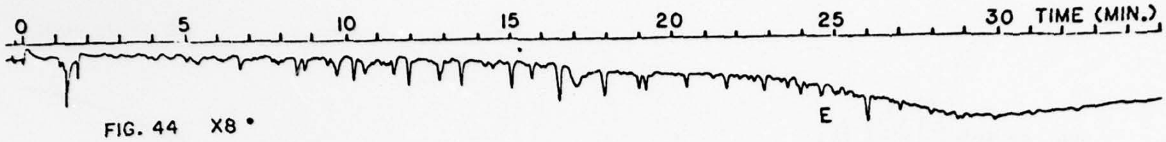
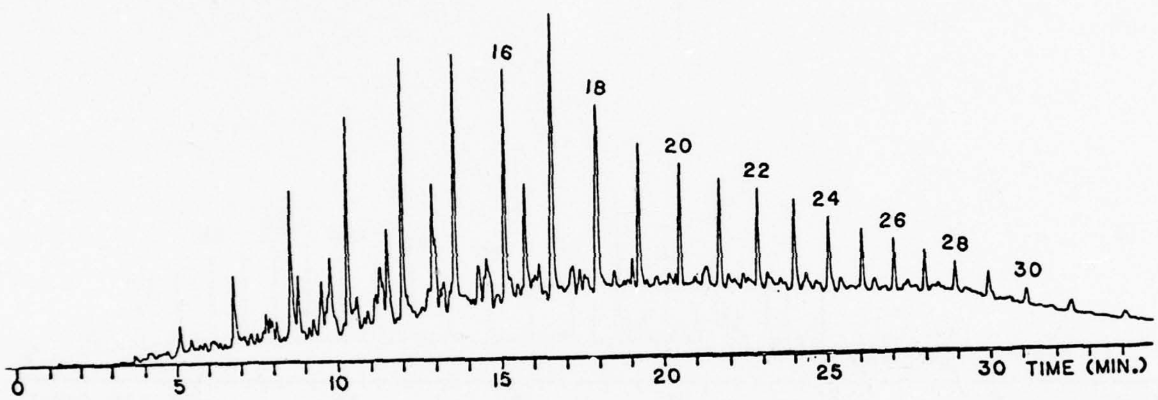


FIG. 44 X8 •
GU-014-CGU
OFFSHORE S. LOUISIANA



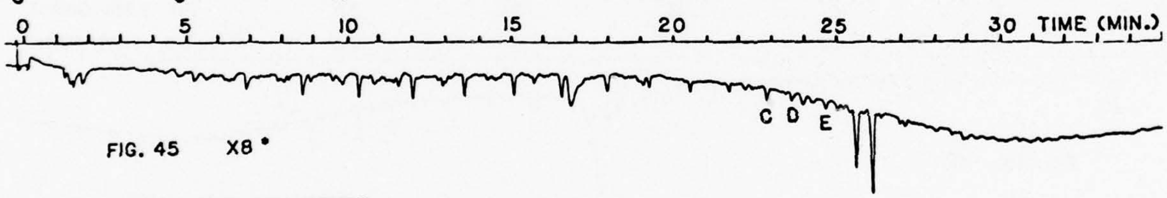
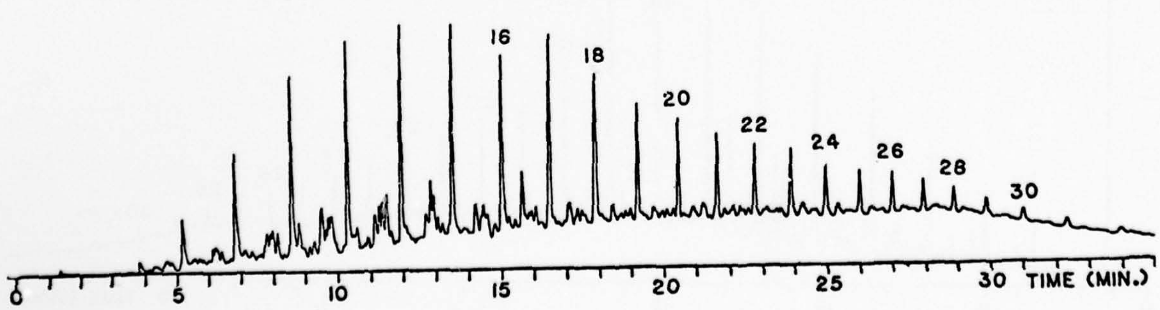


FIG. 45 X8 •

TRIGOM LOUISIANA CRUDE



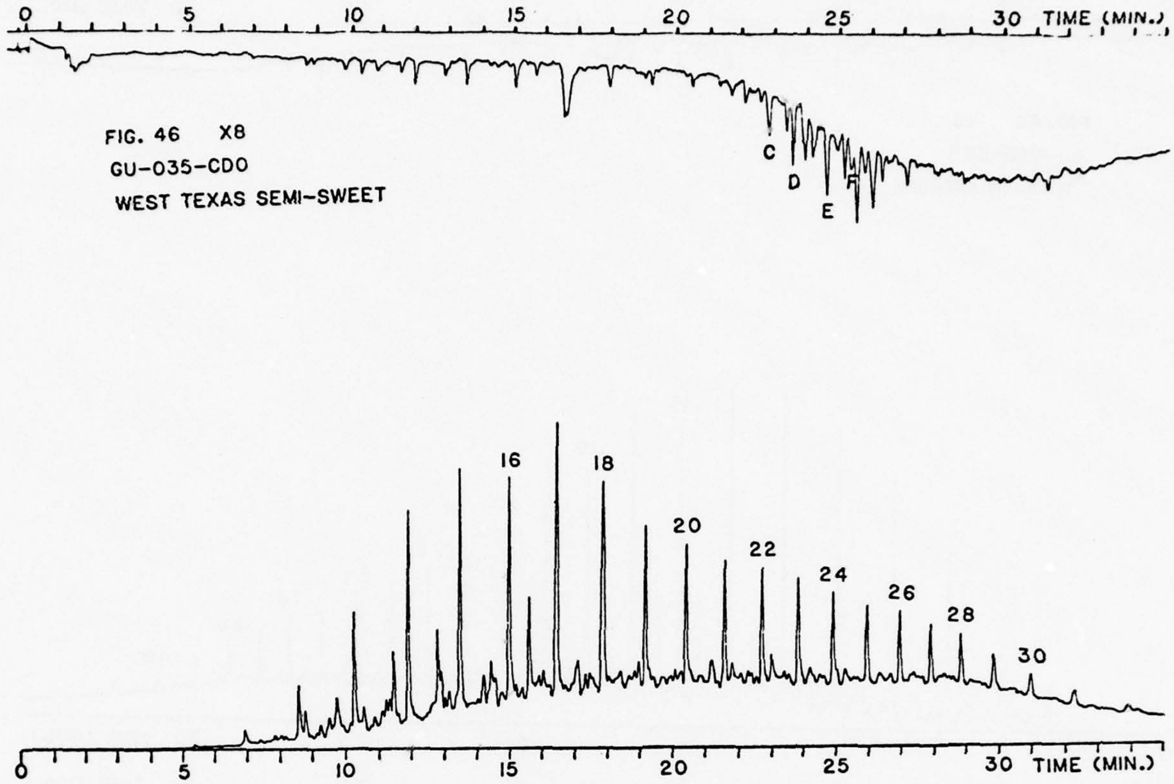


FIG. 46 X8
GU-035-CDO
WEST TEXAS SEMI-SWEET

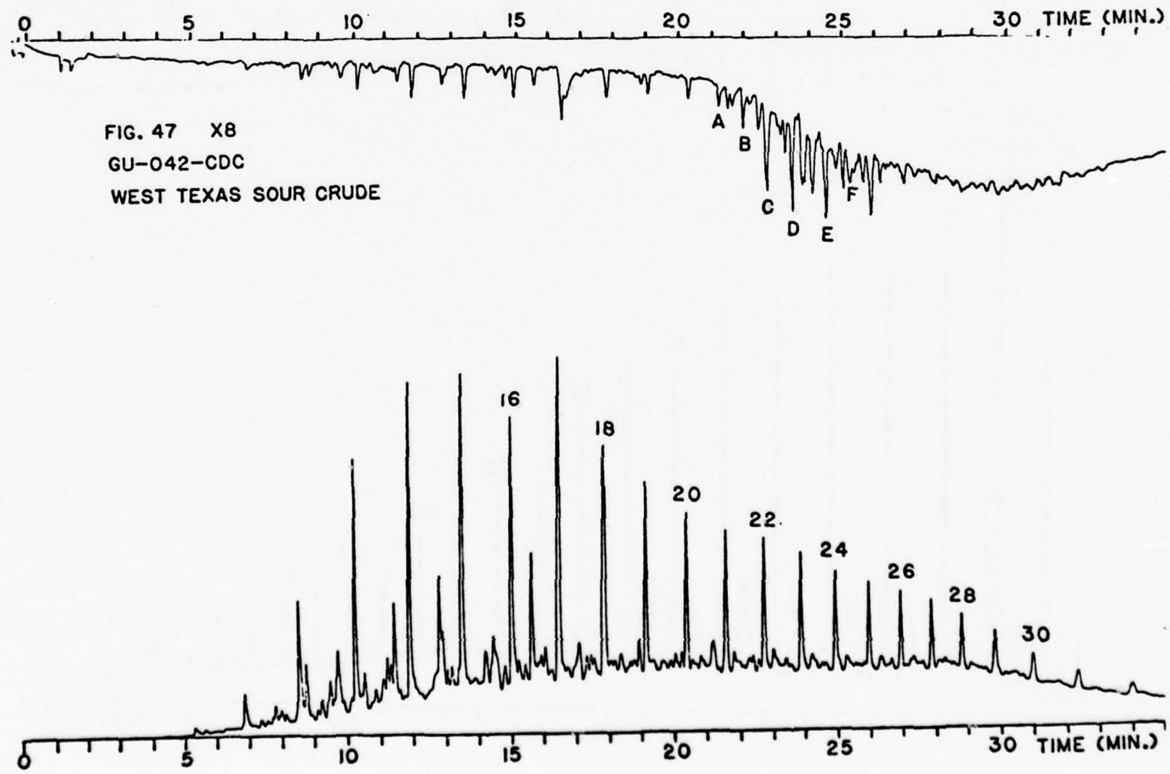


FIG. 47 X8
GU-042-CDC
WEST TEXAS SOUR CRUDE

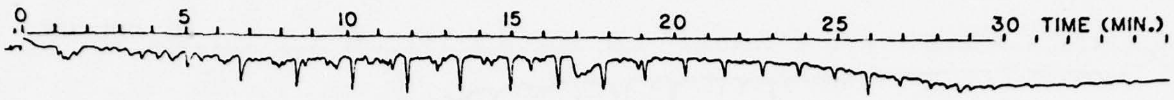
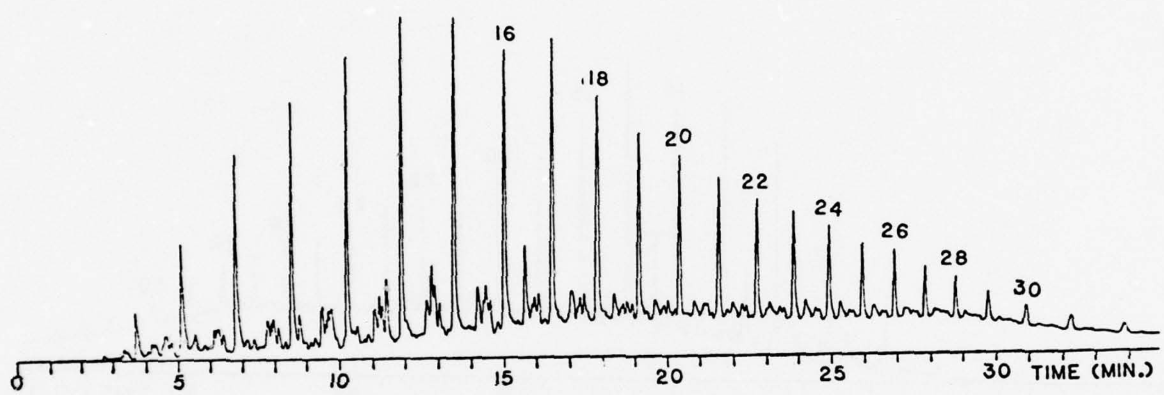


FIG. 48 X8
GU-055-CDO
ALABAMA CITRONELLE



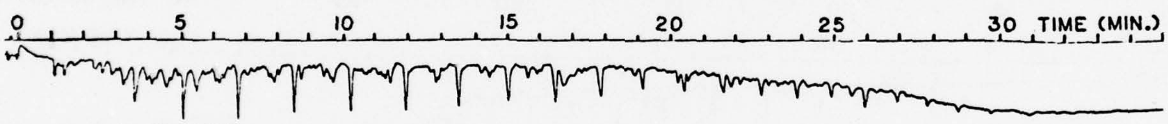
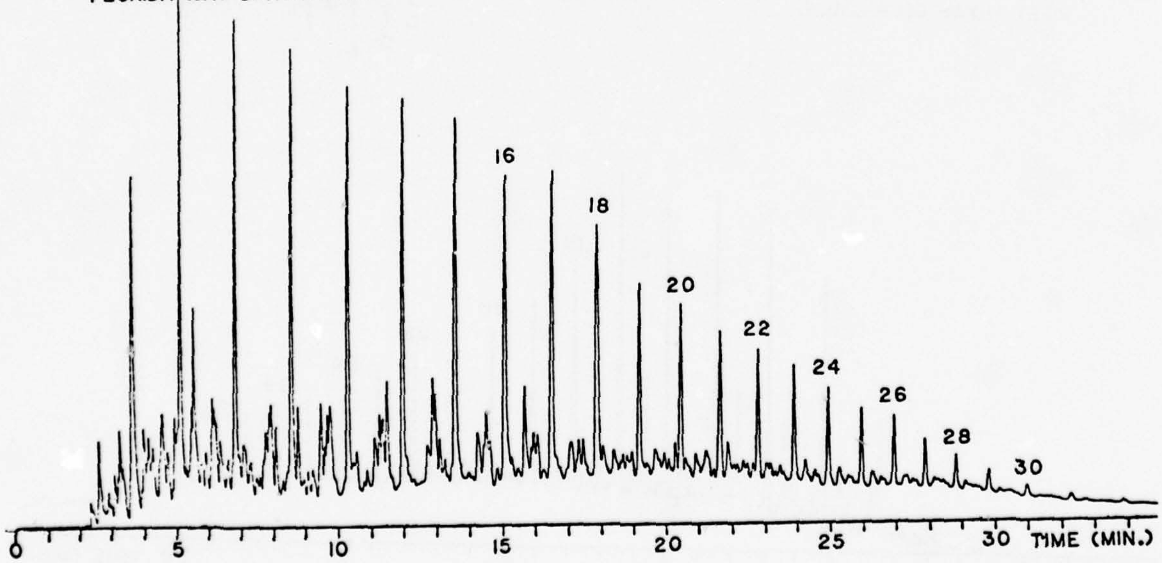


FIG. 49 X8
GU-015-CDO
FLORIDA (JAY SMACKOVER)



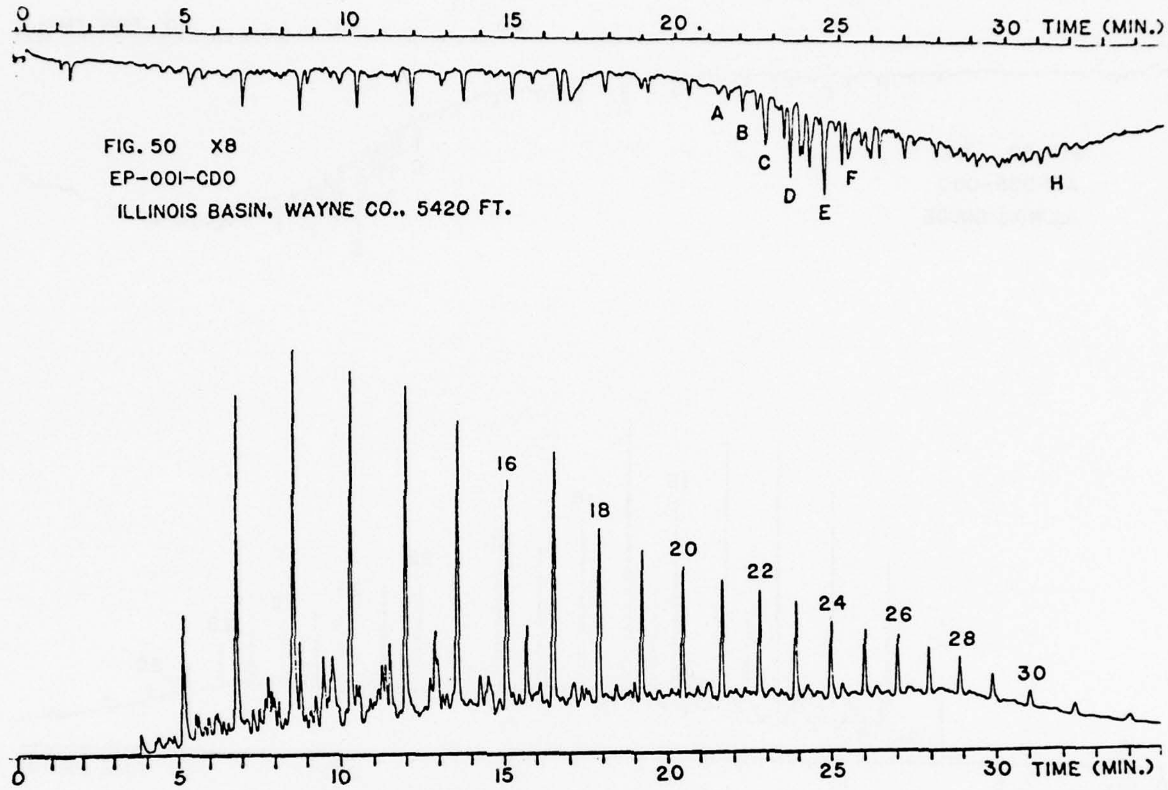


FIG. 50 X8
EP-001-CDO
ILLINOIS BASIN, WAYNE CO., 5420 FT.

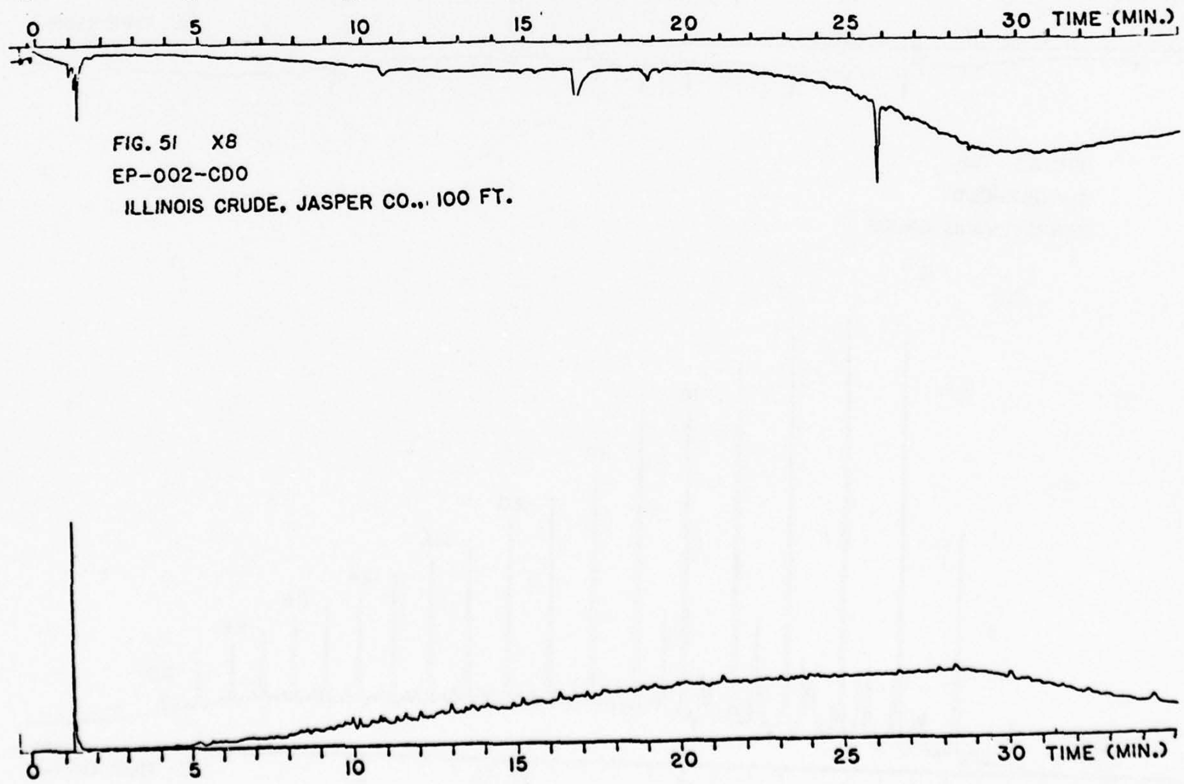


FIG. 51 X8
EP-002-CDO
ILLINOIS CRUDE, JASPER CO., 100 FT.

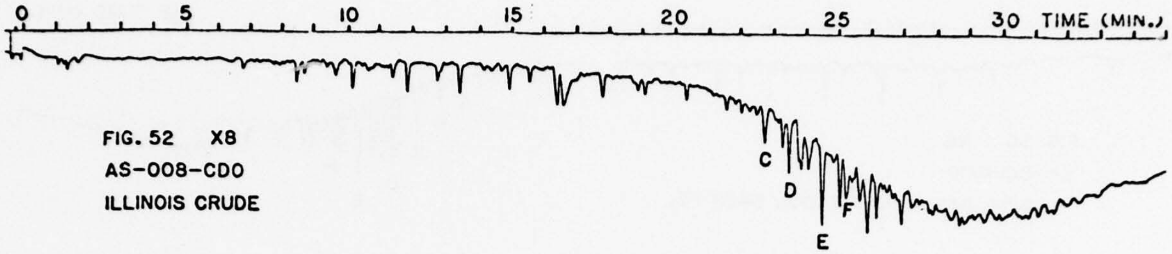
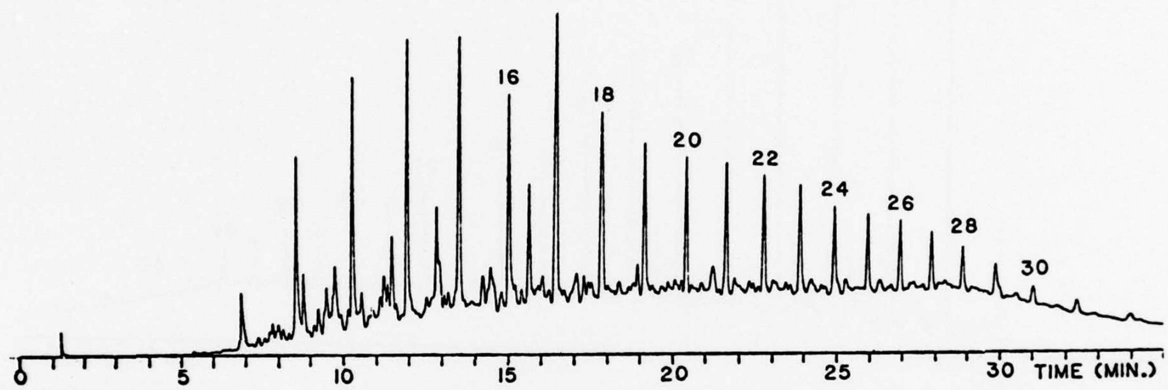


FIG. 52 X8
AS-008-CDO
ILLINOIS CRUDE



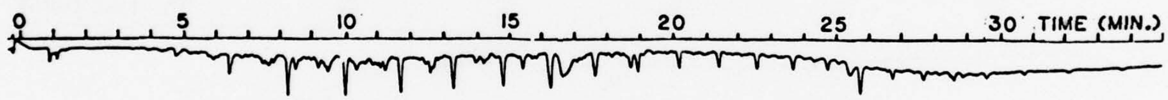
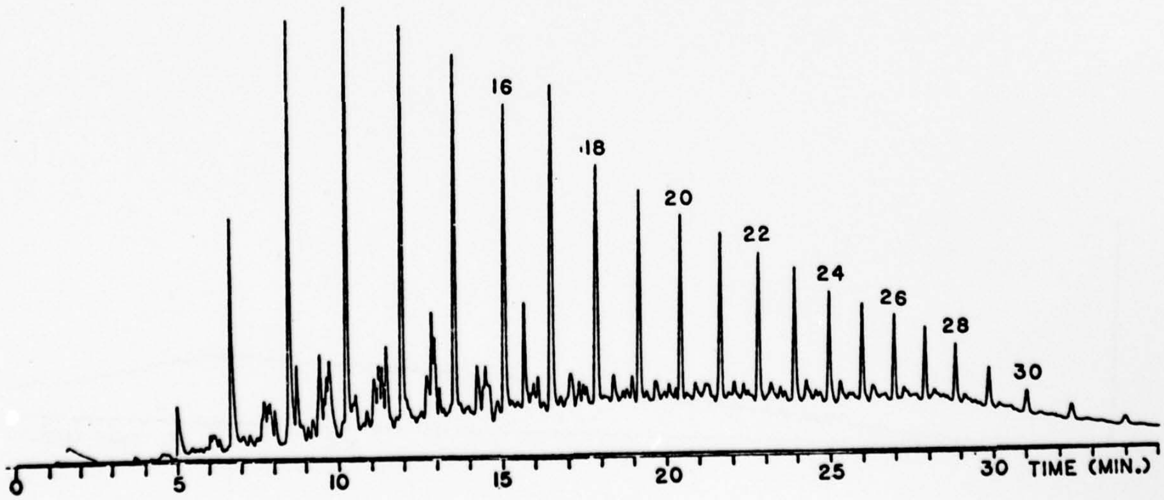


FIG. 53 X8
GU-057-CDO
PENNSYLVANIA CRUDE



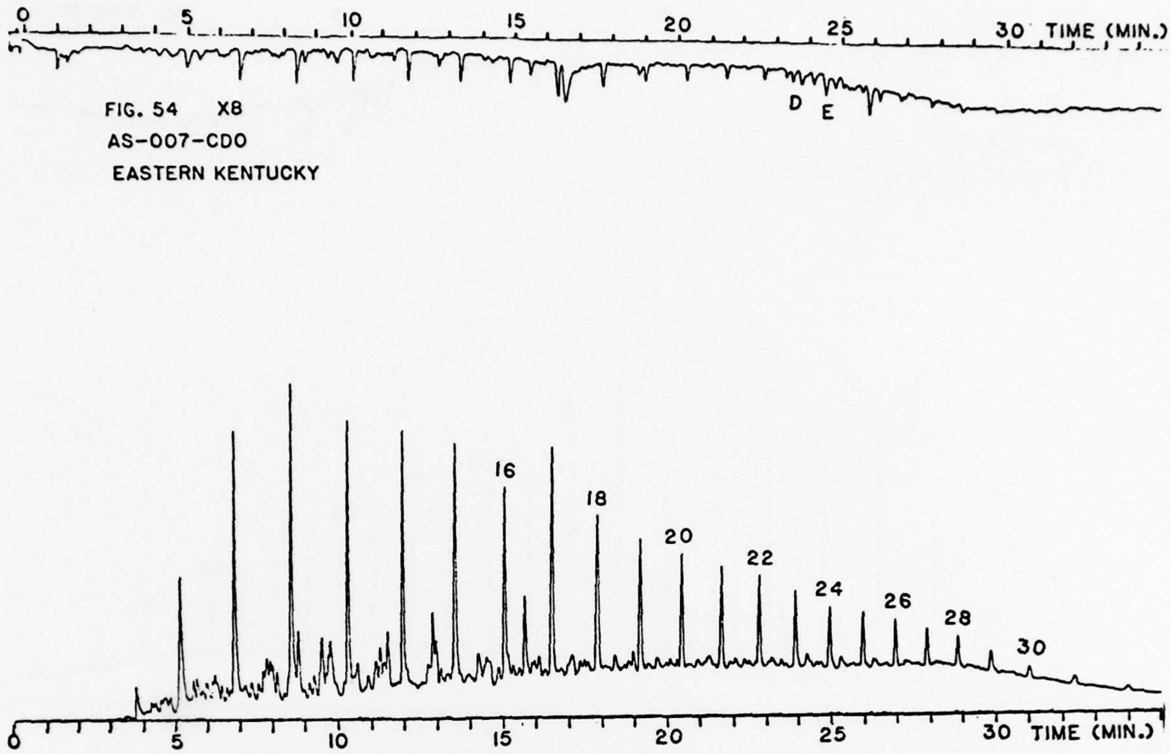


FIG. 54 X8
AS-007-CDO
EASTERN KENTUCKY

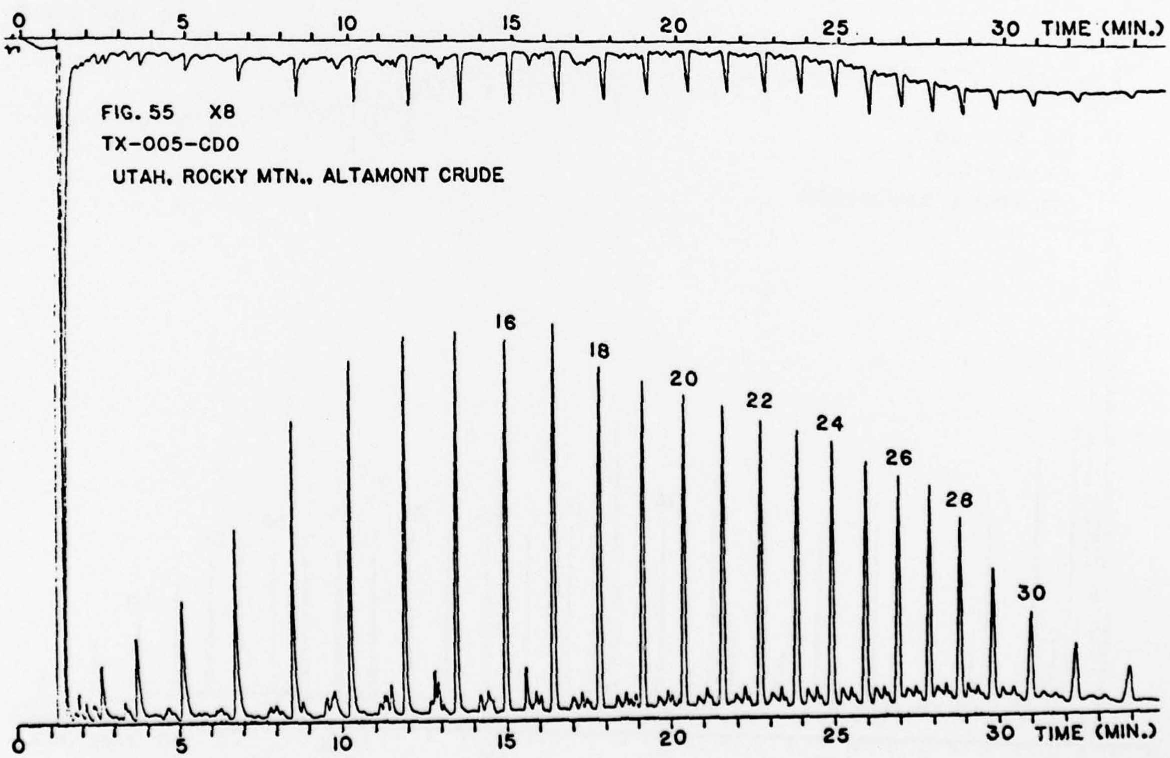


FIG. 55 X8
TX-005-CDO
UTAH, ROCKY MTN., ALTAMONT CRUDE

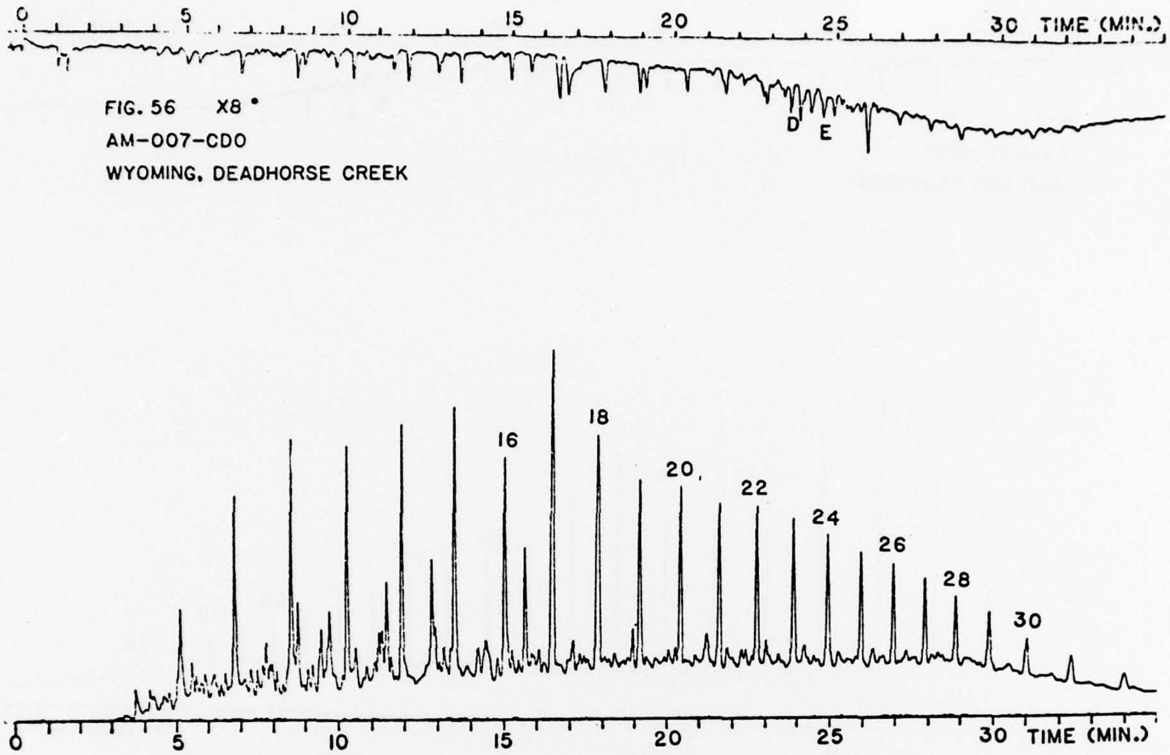


FIG. 56 X8 *
AM-007-CDO
WYOMING, DEADHORSE CREEK

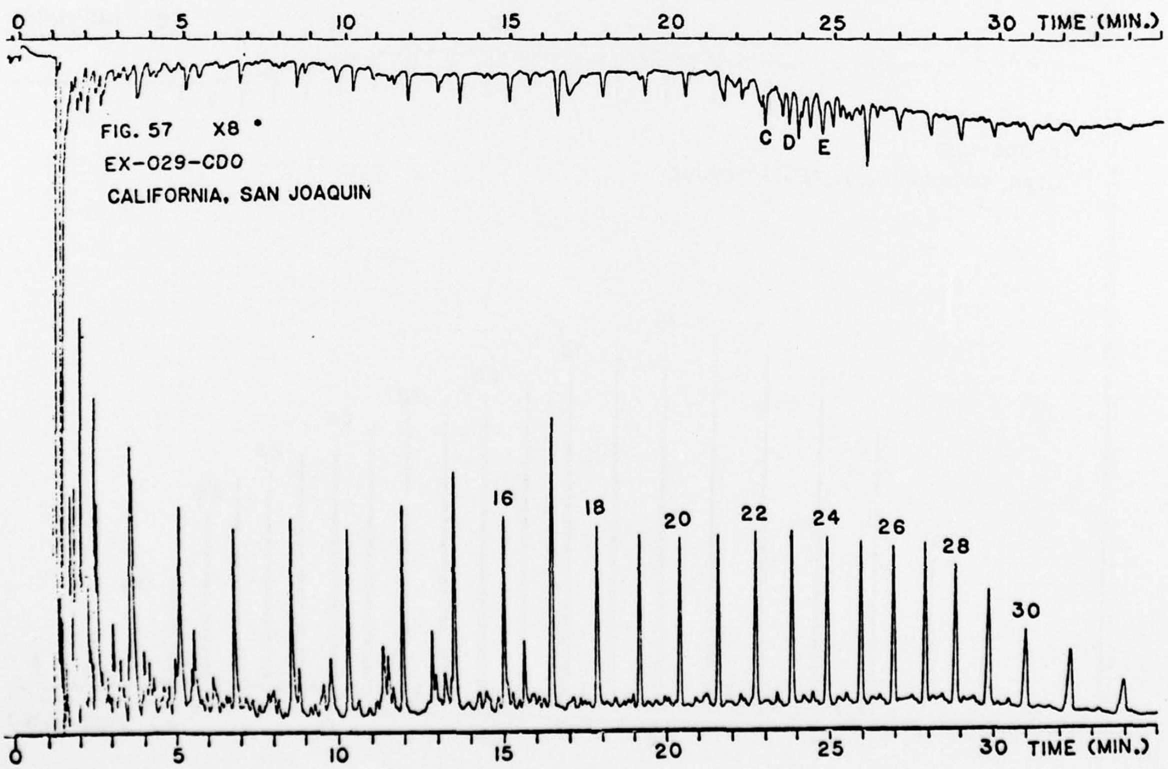


FIG. 57 X8 *
EX-029-CDO
CALIFORNIA, SAN JOAQUIN

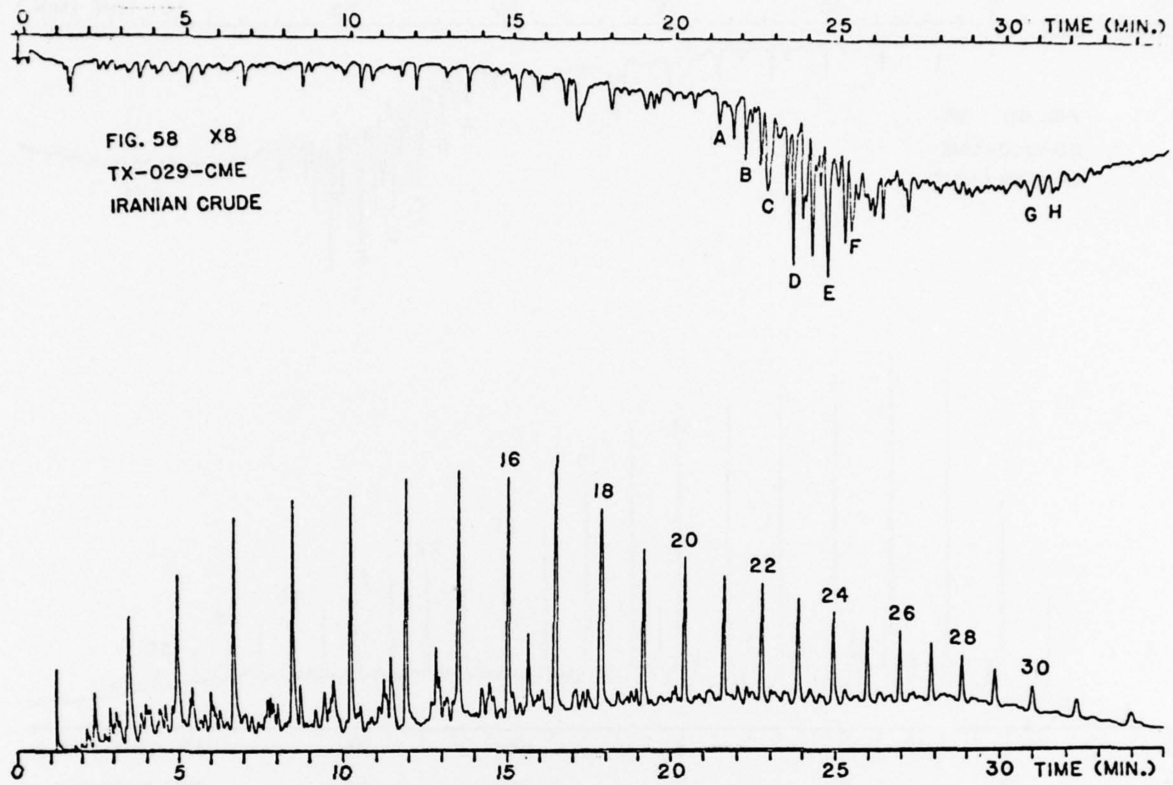


FIG. 58 X8
TX-029-CME
IRANIAN CRUDE
A B C D E F G H
16 18 20 22 24 26 28 30
0 5 10 15 20 25 30 TIME (MIN.)

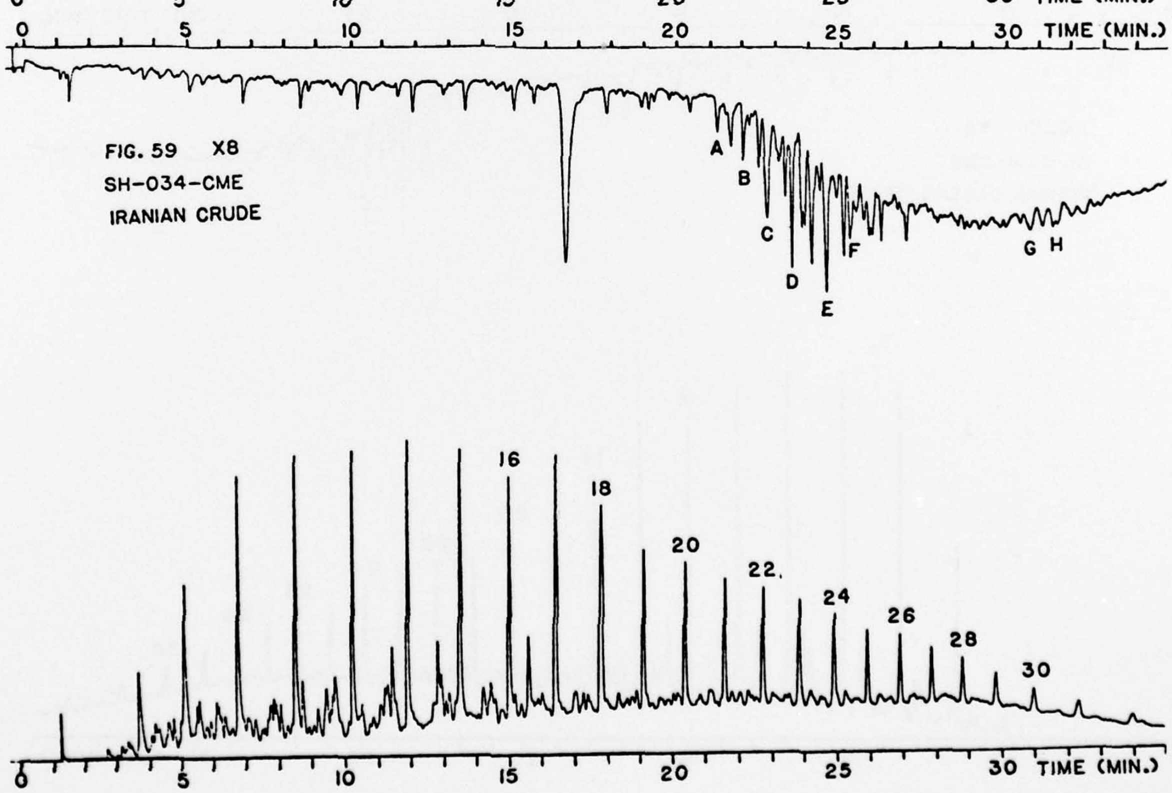


FIG. 59 X8
SH-034-CME
IRANIAN CRUDE
A B C D E F G H
16 18 20 22. 24 26 28 30
0 5 10 15 20 25 30 TIME (MIN.)

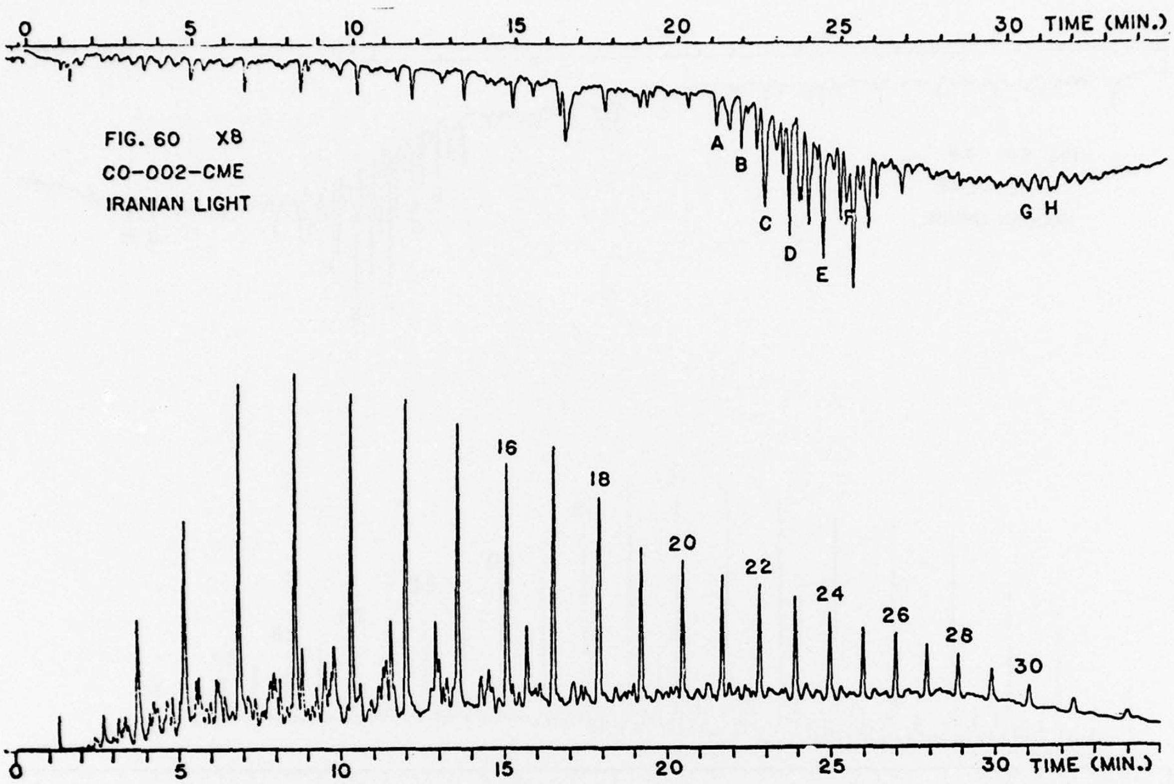


FIG. 60 X8
CO-002-CME
IRANIAN LIGHT

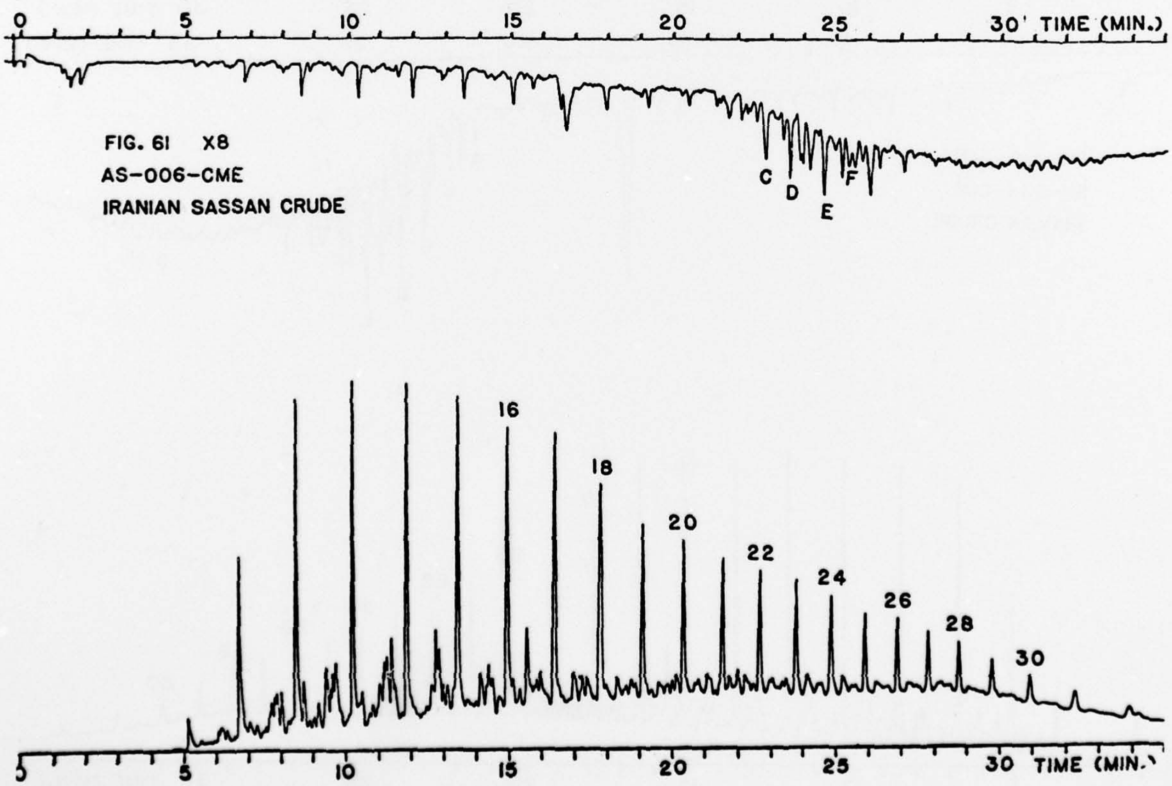


FIG. 61 X8
AS-006-CME
IRANIAN SASSAN CRUDE

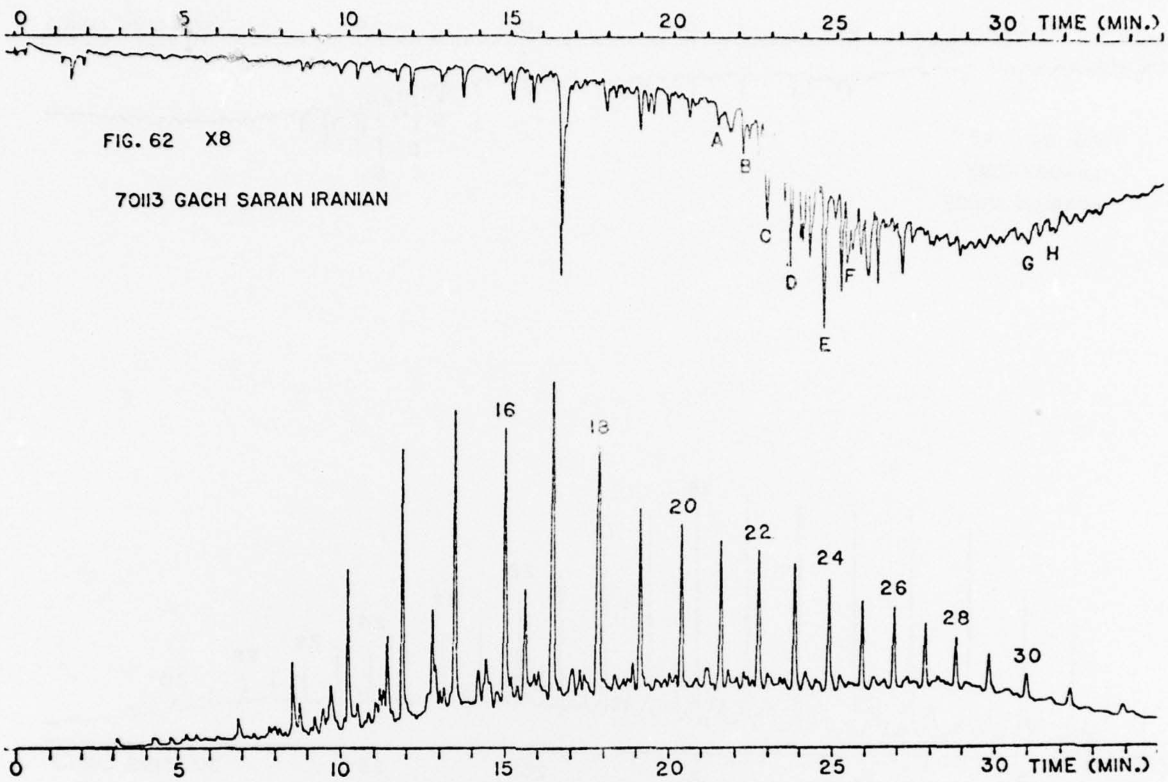


FIG. 62 X8

70113 GACH SARAN IRANIAN

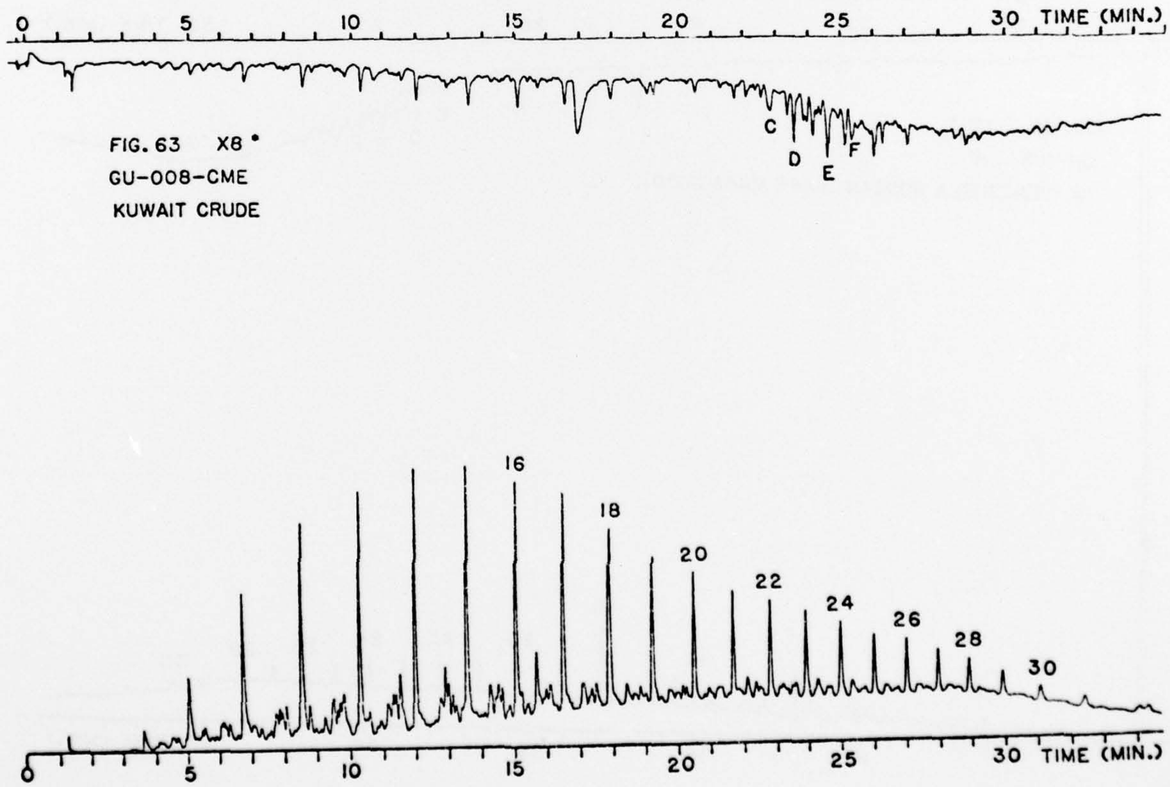


FIG. 63 X8

GU-008-CME

KUWAIT CRUDE

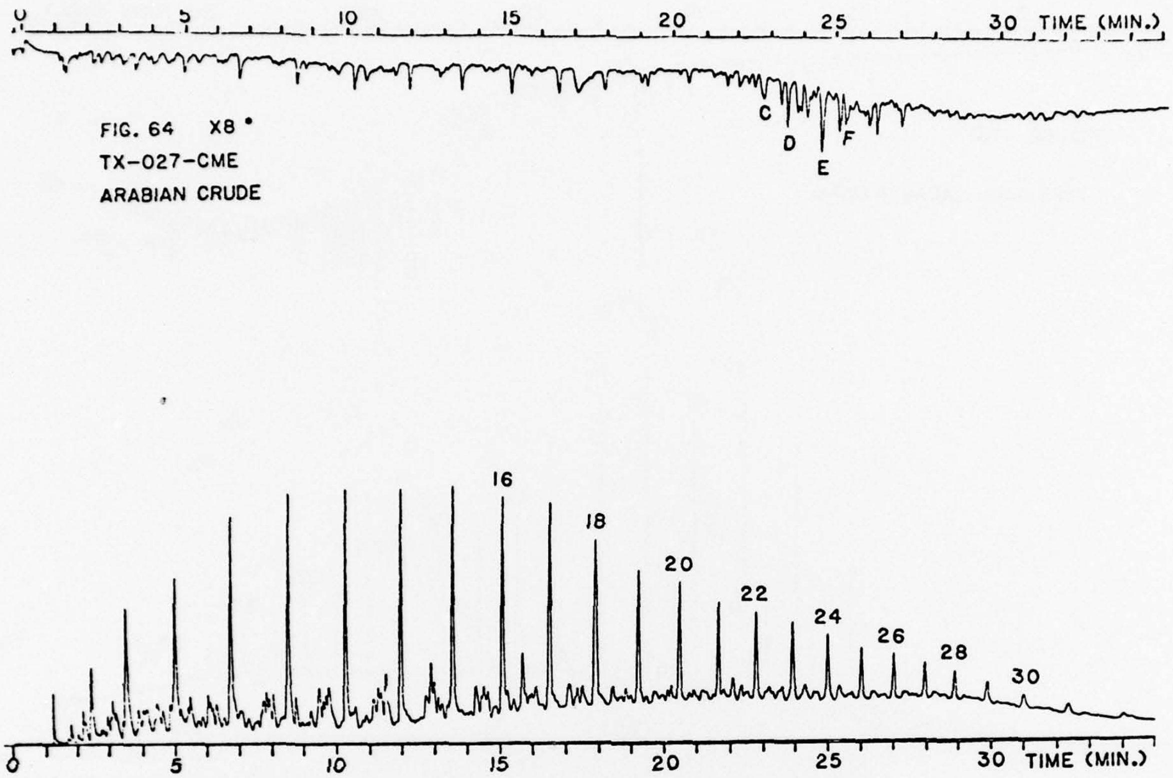


FIG. 64 X8 •
TX-027-CME
ARABIAN CRUDE

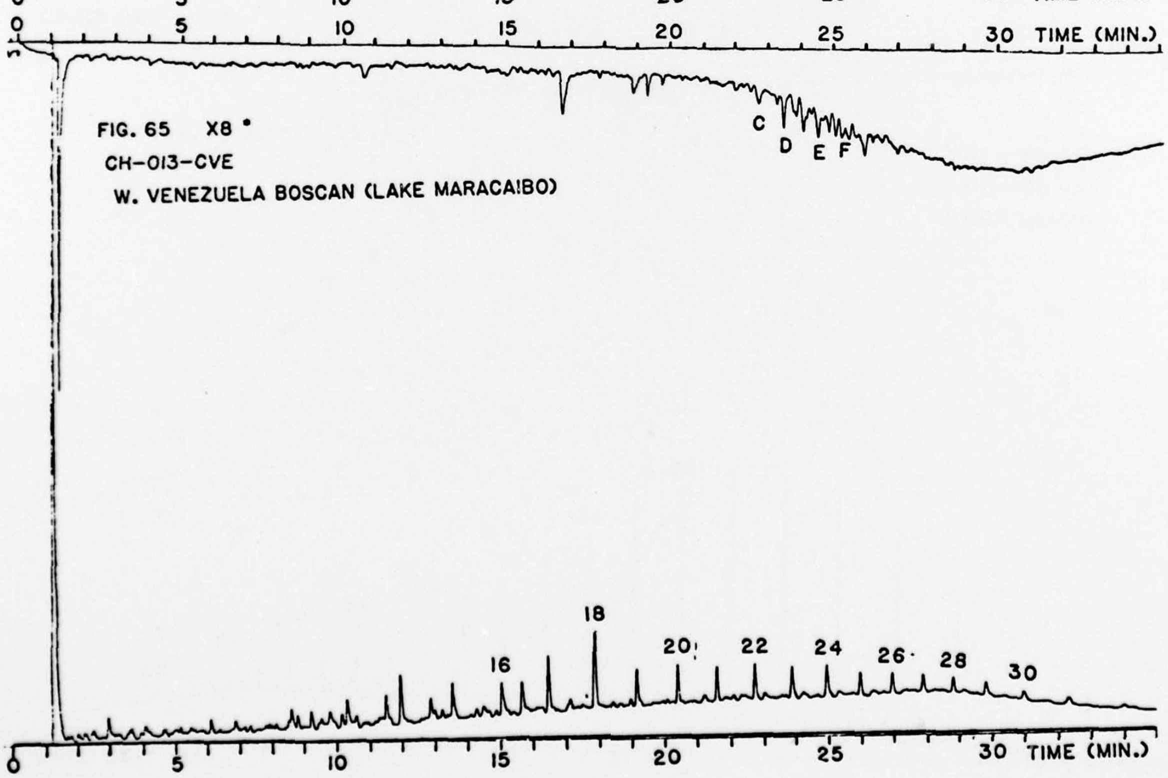


FIG. 65 X8 •
CH-013-CVE
W. VENEZUELA BOSCAN (LAKE MARACAIBO)

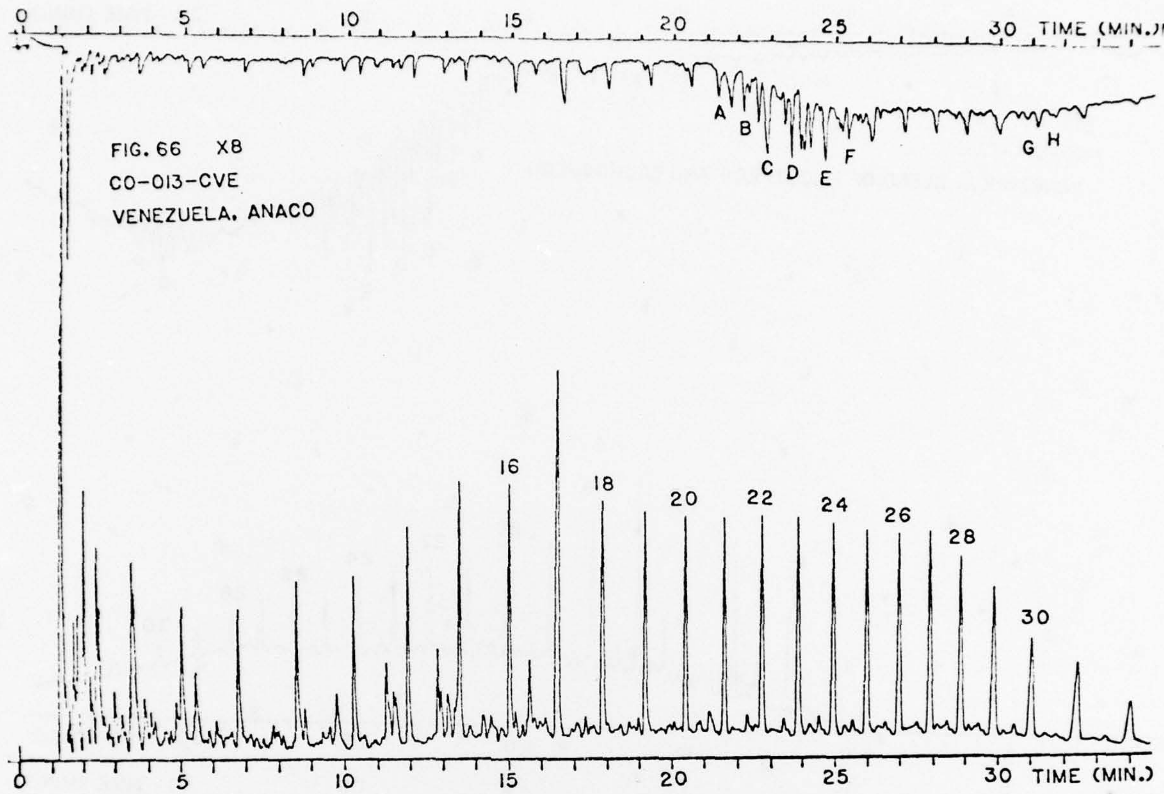


FIG. 66 X8
CO-013-CVE
VENEZUELA, ANACO

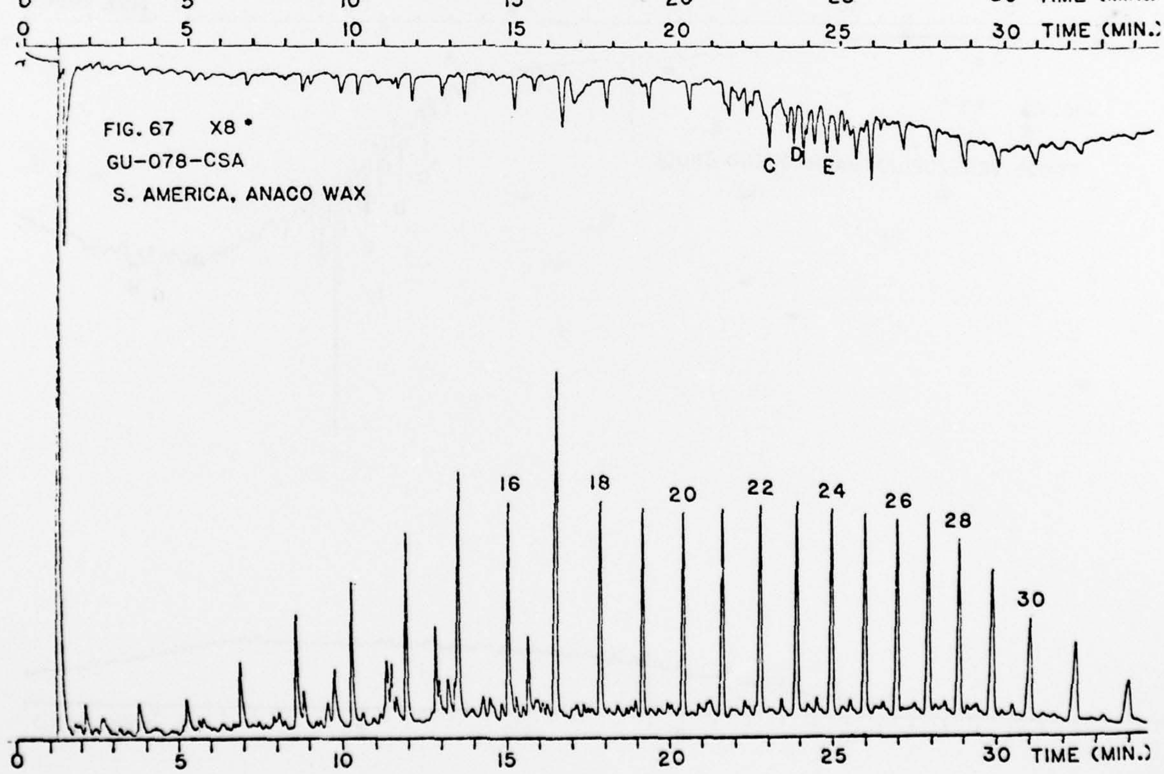


FIG. 67 X8
GU-078-CSA
S. AMERICA, ANACO WAX

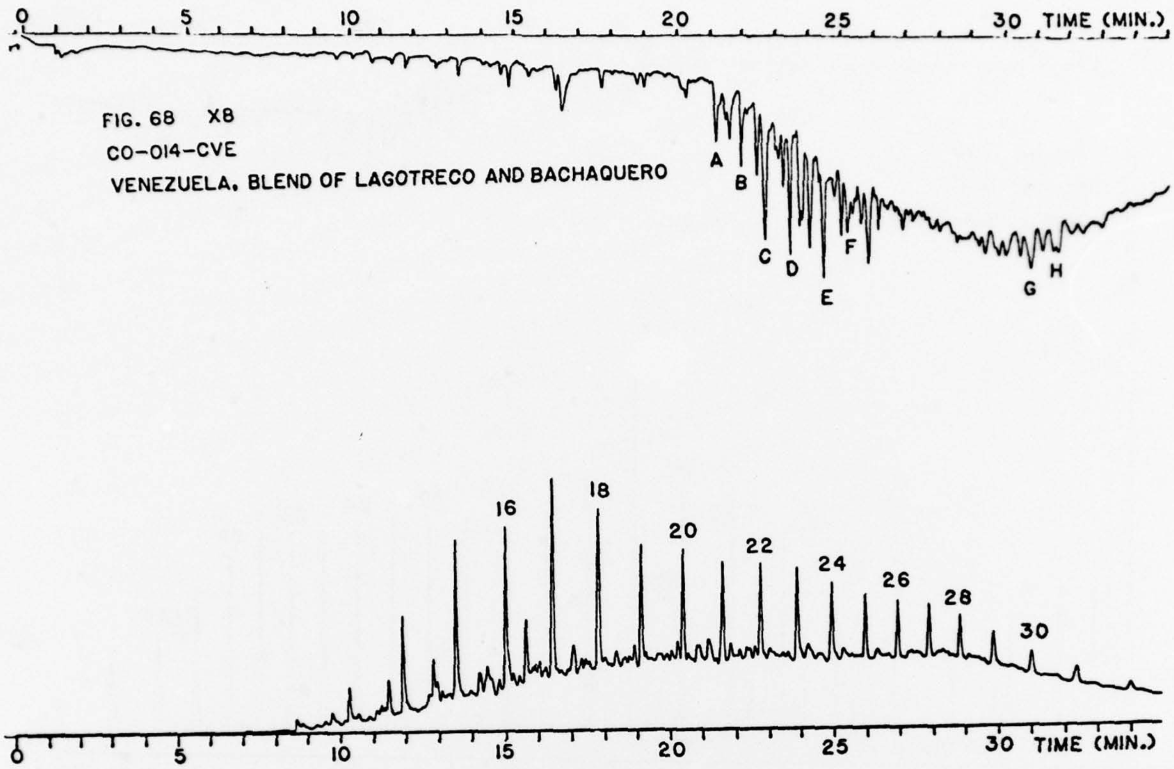


FIG. 68 X8
CO-014-CVE
VENEZUELA, BLEND OF LAGOTRECO AND BACHAQUERO

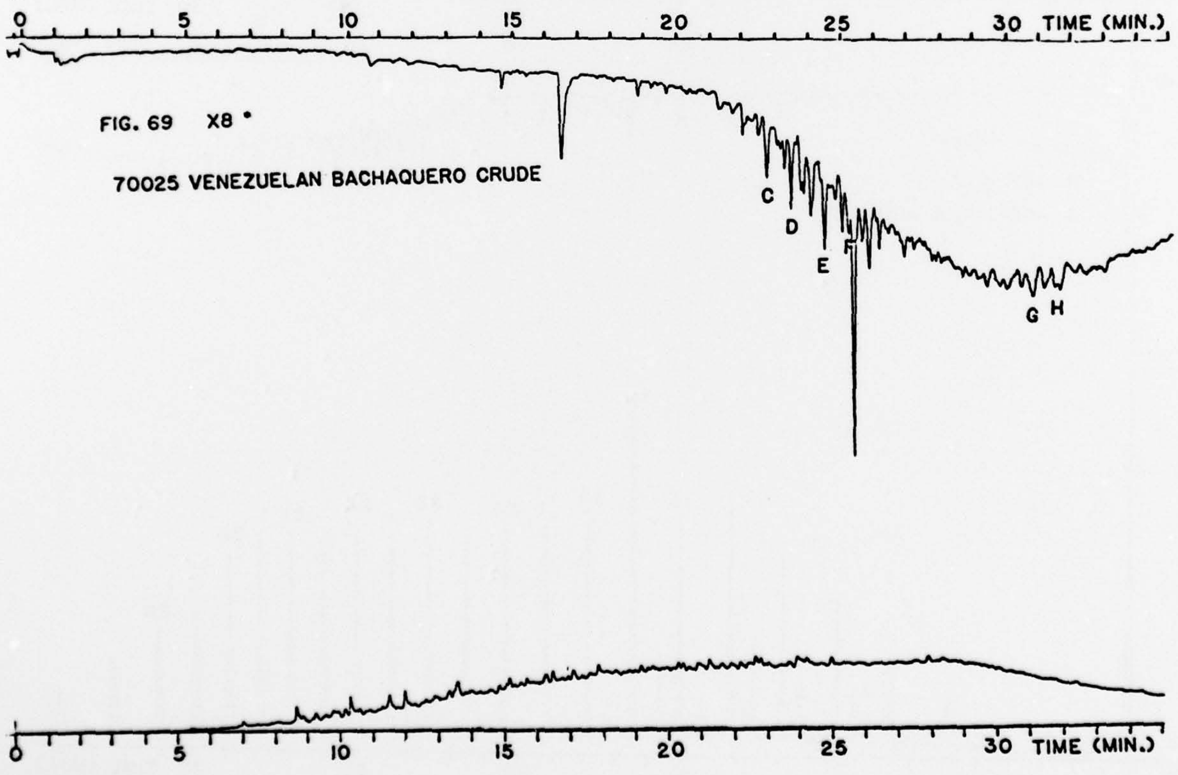


FIG. 69 X8
70025 VENEZUELAN BACHAQUERO CRUDE

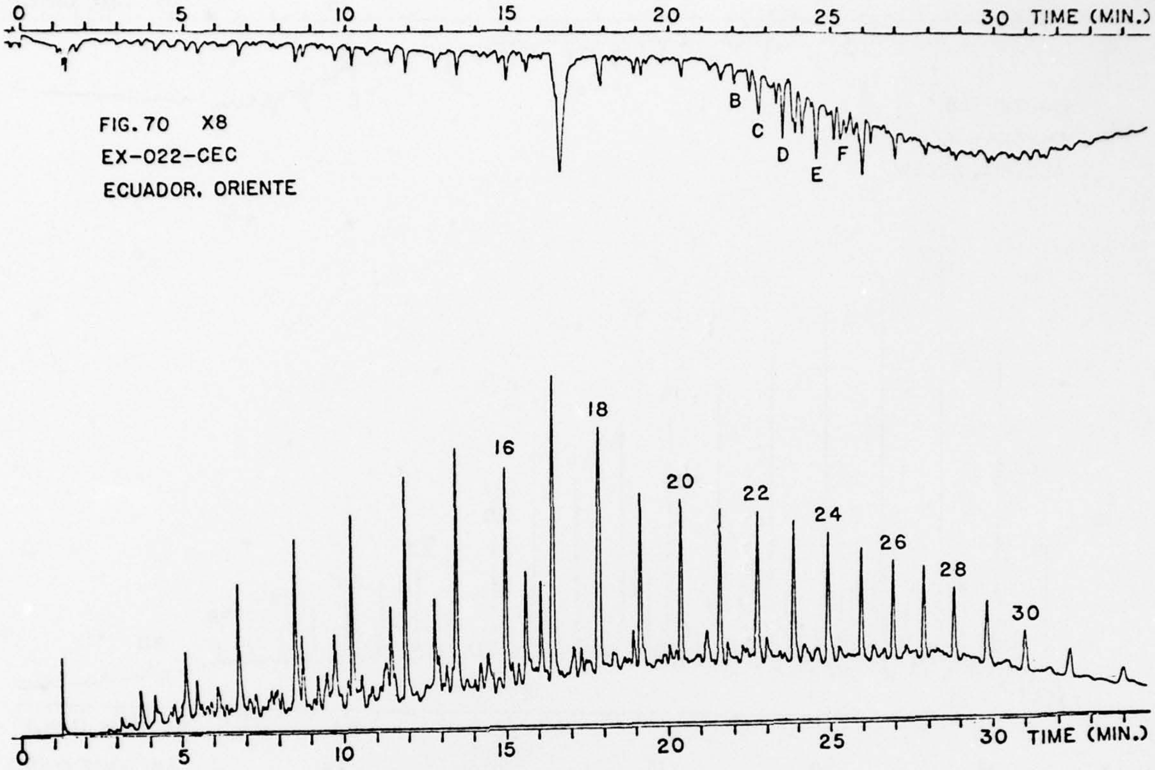


FIG. 70 X8
EX-022-CEC
ECUADOR, ORIENTE

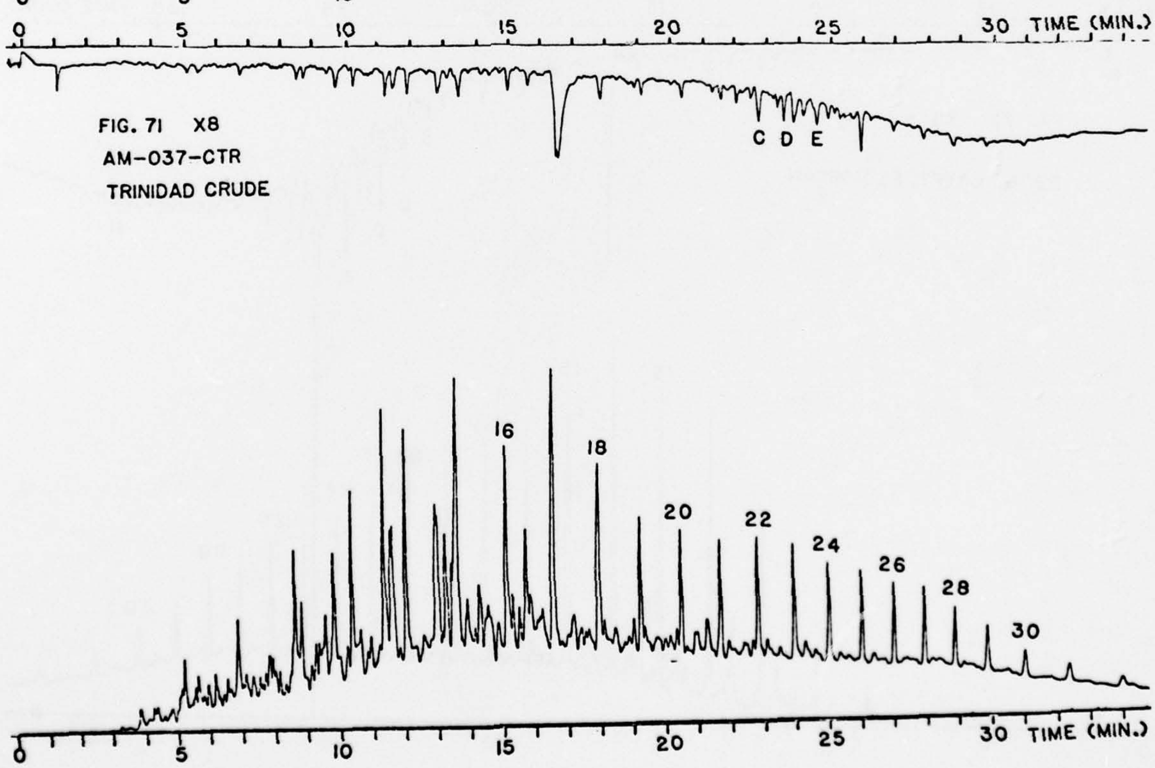
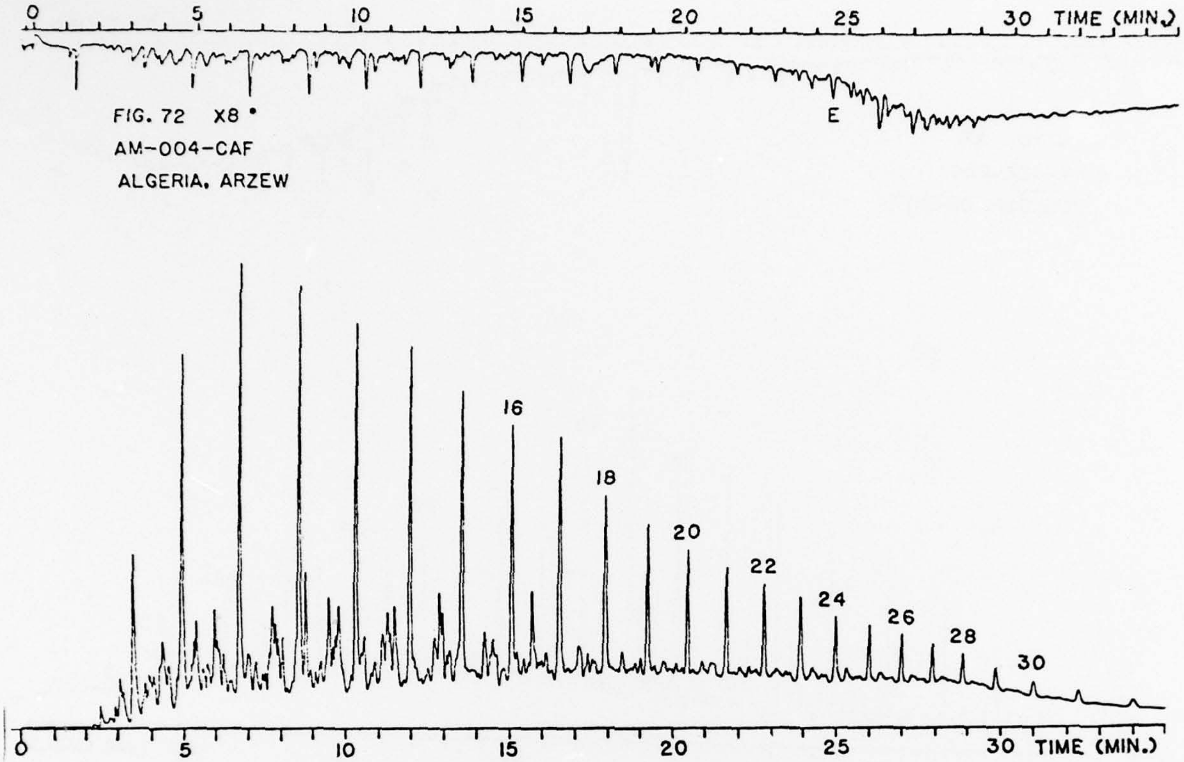
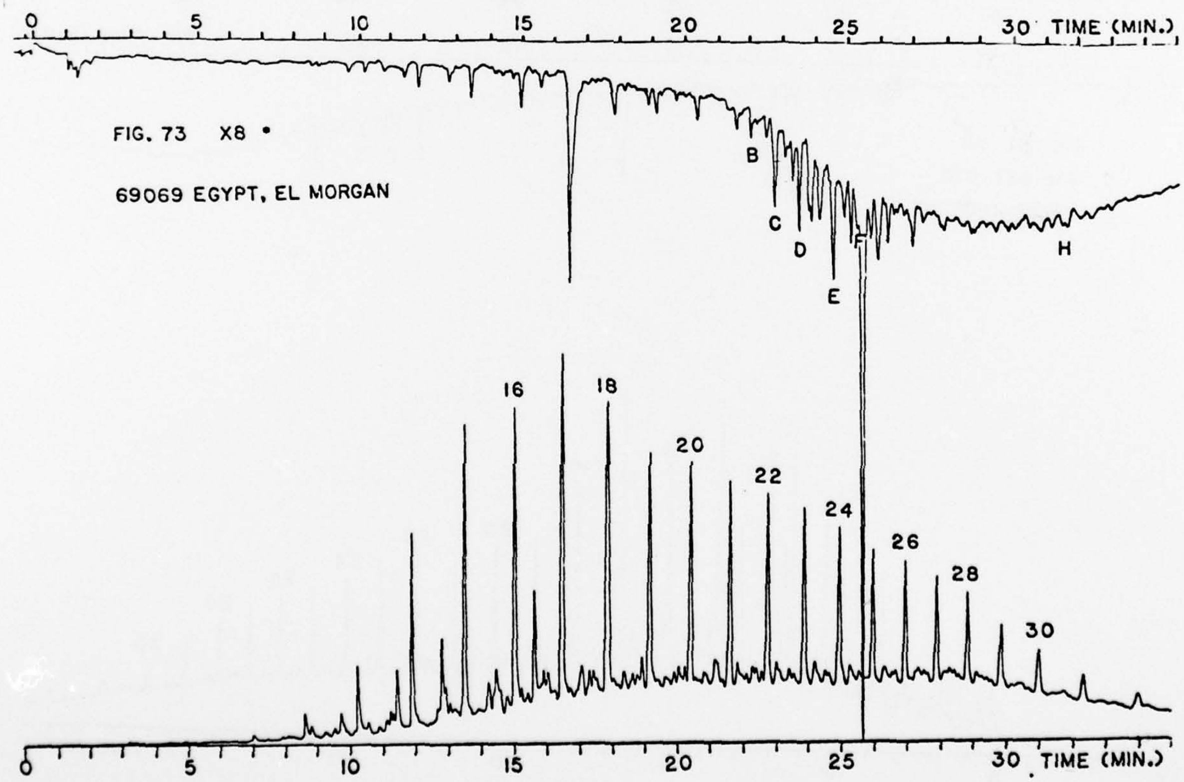


FIG. 71 X8
AM-037-CTR
TRINIDAD CRUDE


0 5 10 15 20 25 30 TIME (MIN.)
FIG. 72 X8 •
AM-004-CAF
ALGERIA, ARZEW
E
16
18
20
22
24
26
28
30
0 5 10 15 20 25 30 TIME (MIN.)


0 5 10 15 20 25 30 TIME (MIN.)
FIG. 73 X8 •
69069 EGYPT, EL MORGAN
B
C
D
E
F
H
16
18
20
22
24
26
28
30
0 5 10 15 20 25 30 TIME (MIN.)

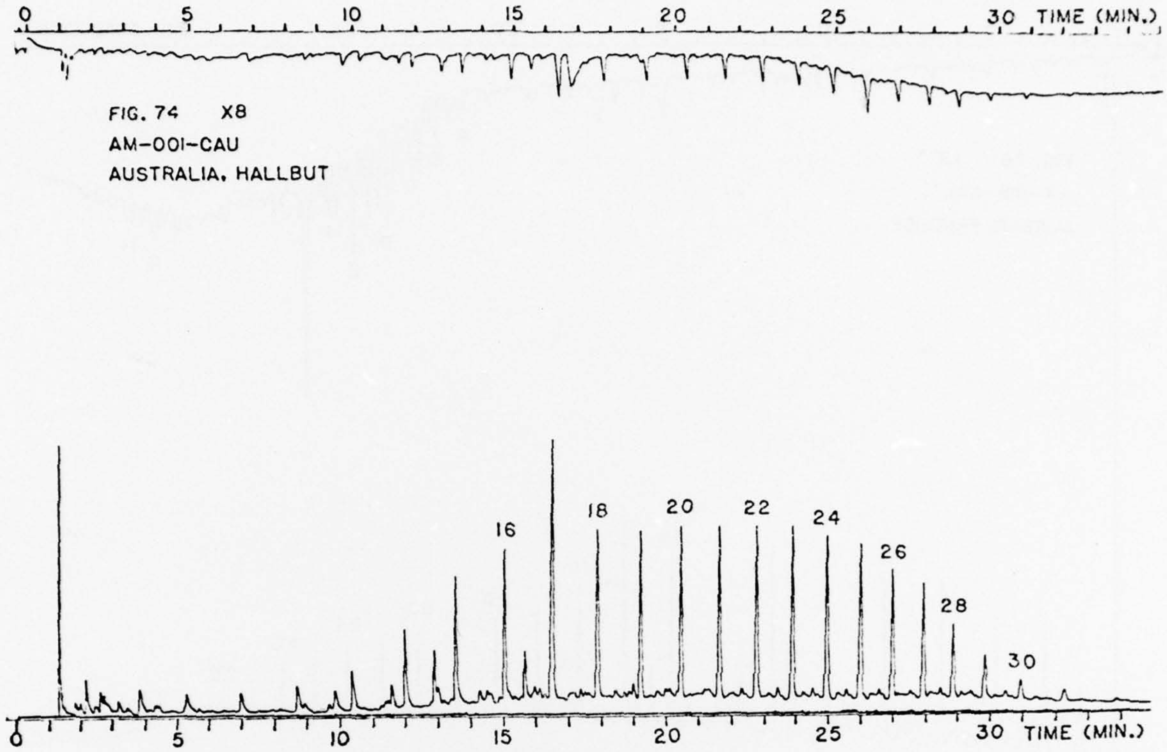


FIG. 74 X8
AM-001-CAU
AUSTRALIA, HALLBUT

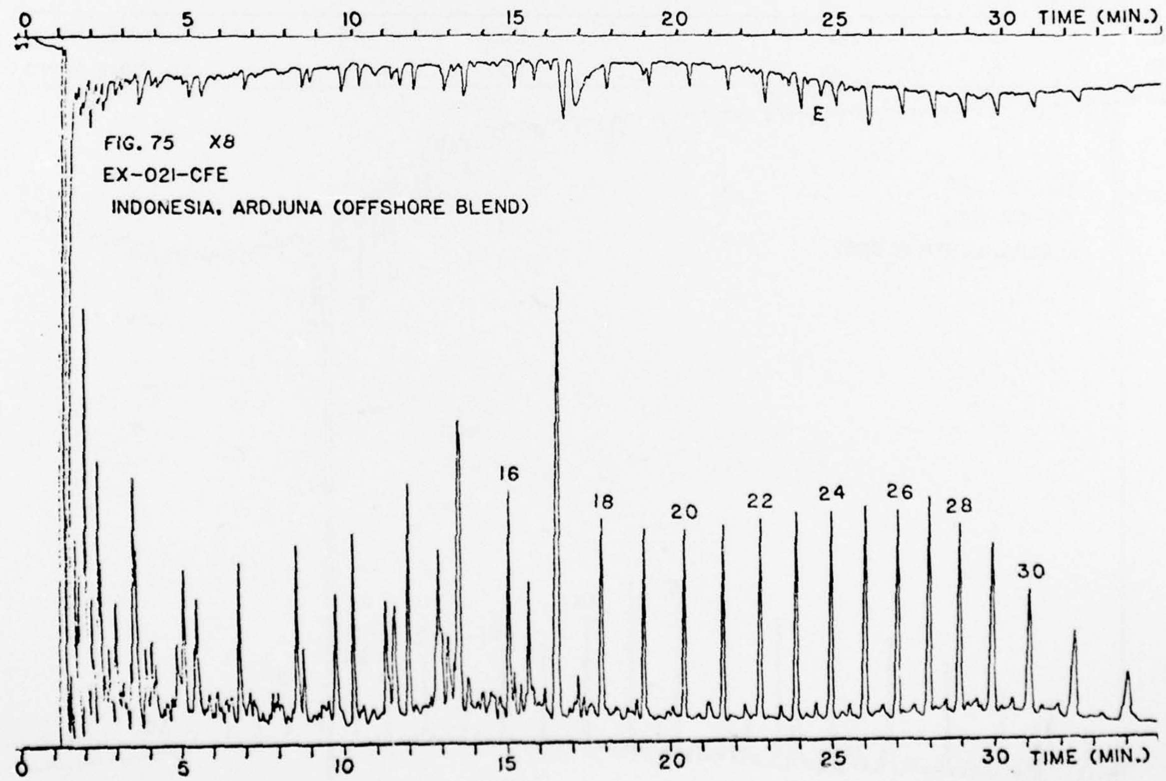


FIG. 75 X8
EX-021-CFE
INDONESIA, ARDJUNA (OFFSHORE BLEND)

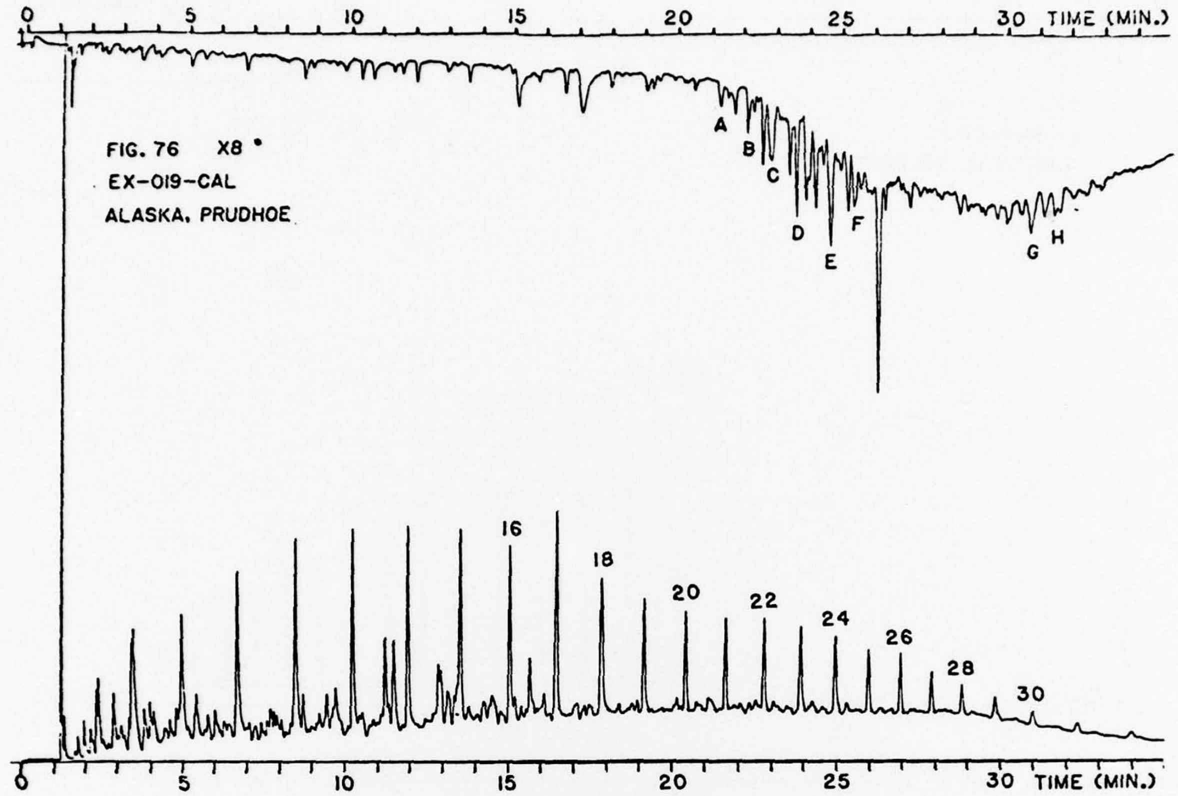


FIG. 76 X8
EX-019-CAL
ALASKA, PRUDHOE
A
B
C
D
E
F
G
H
16
18
20
22
24
26
28
30
0
5
10
15
20
25
30
TIME (MIN.)

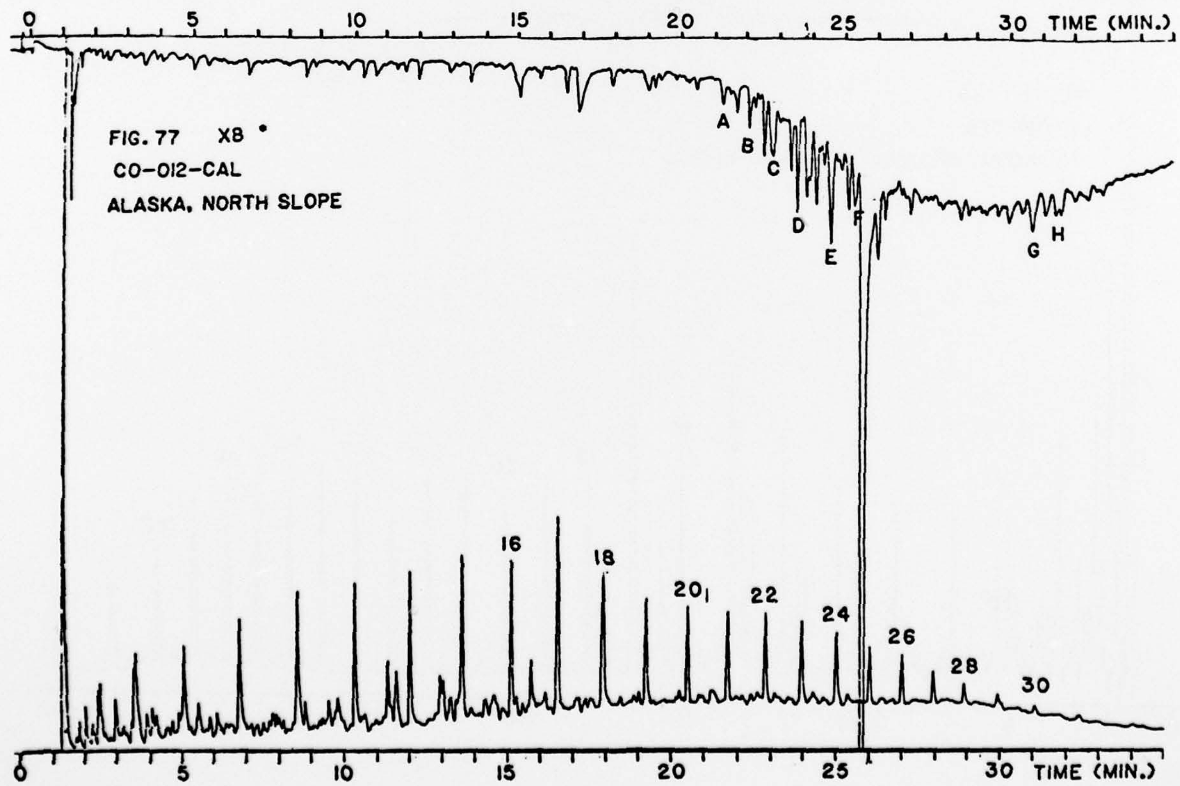
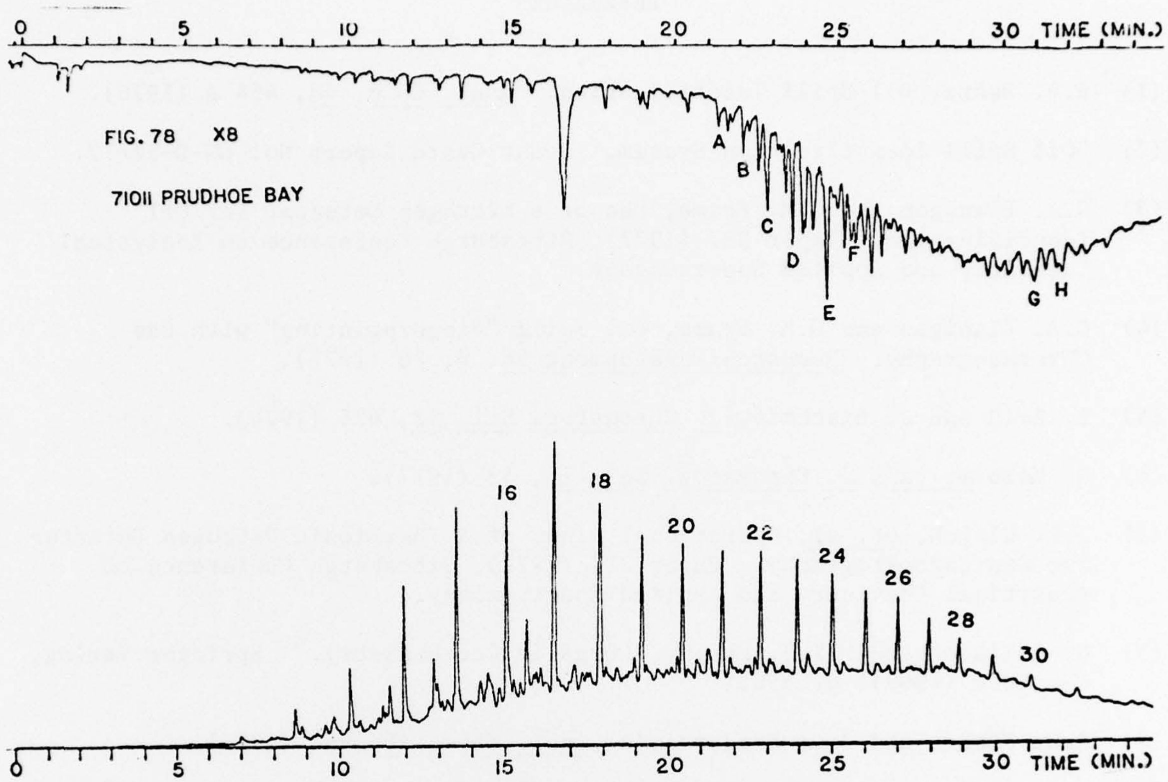
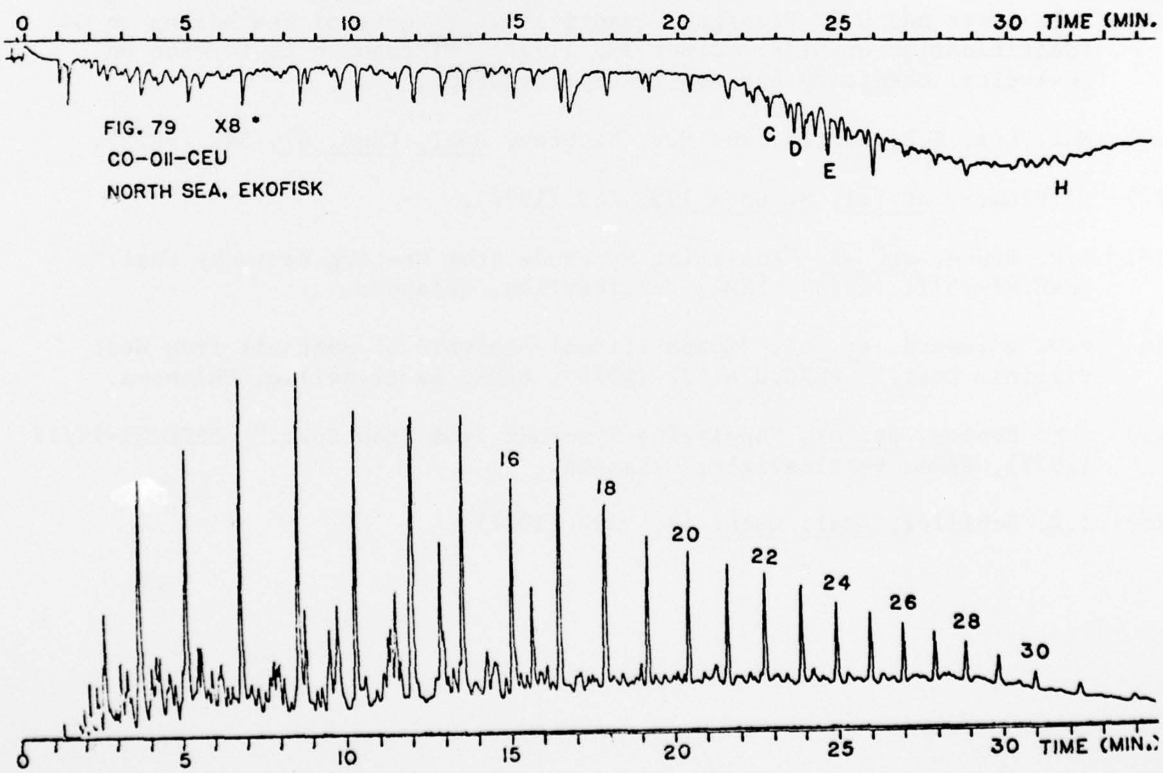


FIG. 77 X8
CO-012-CAL
ALASKA, NORTH SLOPE
A
B
C
D
E
F
G
H
16
18
20
22
24
26
28
30
0
5
10
15
20
25
30
TIME (MIN.)



0 5 10 15 20 25 30 TIME (MIN.)
FIG. 78 X8
71011 PRUDHOE BAY
A
B
C
D
E
F
G H
16
18
20
22
24
26
28
30
0 5 10 15 20 25 30 TIME (MIN.)



0 5 10 15 20 25 30 TIME (MIN.
FIG. 79 X8
CO-011-CEU
NORTH SEA, EKOFISK
C
D
E
H
16
18
20
22
24
26
28
30
0 5 10 15 20 25 30 TIME (MIN.)

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